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# Guidelines for Field Testing Aquatic Fate and Transport Models

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# GUIDELINES FOR FIELD TESTING AQUATIC FATE AND TRANSPORT MODELS: FINAL REPORT

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This guidance has been developed for those attempting to field validate aquatic fate and transport models. Included are discussions of the major steps in validating models and sections on the individual fate and transport processes: biodegradation, oxidation, hydrolysis, photolysis, ionization, sorption, bioconcentration, volatilization, and physical transport. For each process the following information is provided: a general description of the process, a list and discussion of environmental factors affecting the process, a list of the priority pollutants for which the process is important, a list of model-specific environmental inputs, and field methods for collecting these input data.

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# ABSTRACT

This guidance has been developed for the EPA's Office of Pesticides and Toxic Substances (OPTS) to aid in field validation of aquatic fate and transport models. The OPTS anticipates that several potentially useful models will need to be validated for application to a variety of compartmental aquatic fate and transport models, and, therefore, the guidance is general. The guidelines are not a set of "cookbook" instructions but rather discussions of the major steps in model validation, field plan development, and data interpretation. They also include overviews of environmental fate processes and a discussion of specific field sampling methods.

Validation of a model is defined in this report as a comparison of model results with numerical data derived from observations of the environment. Complete model validation requires testing over the full range of conditions for which predictions are intended. At a minimum, this requires a series of validations in various aquatic environments (streams, lakes, estuaries), with chemicals that typify the major fate and transport processes (biotransformation, hydrolysis, oxidation, photolysis, sorption, ionization, volatilization, bioconcentration, and physical transport). Validated models are useful in the regulatory process because they withstand scientific scrutiny and are defensible in courts of law. However, models are ultimately judged by their usefulness to the user rather than against a scientific standard. Thus, by this definition, a model may be valid for one use but invalid for another.

Fate and transport models may be based upon either an empirical approach or a theoretical approach that considers transport and fate processes. Empirical models which are based on extensive field observation are usually calibrated to specific existing sites and chemicals and provide no rational basis for making predictions outside their range of prior observation. Thus, models of this type are generally not suited for predicting the fate of new chemicals and are not considered in these guidelines.

The theoretical approach is based upon an understanding of environmental fate and transport processes. This type of model is considerably more versatile since it is designed to predict environmental fate and pollutant concentrations based upon degradation rate constants and relatively simple chemical and environmental input data. Therefore, theoretical models can be applied to chemicals which haven't yet been introduced into the environment. Such models are of considerable interest to the U.S. Environmental Protection Agency and in particular, the OPTS.

This guidance is designed to be useful in validating a variety of models but is largely based upon experience gained during field validations of the EXAMS model. Validations of this model were conducted and this experience used to modify and improve the document. Included in the document are

discussions of the major steps in validating models and sections on the individual fate and transport processes. For each process the following information is provided: a general description of the process, a list and discussion of environmental factors affecting the process, a list of the priority pollutants for which the process is important, a list of model-specific environmental inputs, and field methods for collecting these input data.

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# INTRODUCTION

Aquatic fate and transport models are being developed that predict the fate and concentration of chemicals in natural waters. Such models may be based upon either an empirical approach or a theoretical approach that considers transport and fate processes. Empirical models are based on extensive field observation, usually calibrated to specific existing sites and chemicals, and provide no rational basis for making predictions outside their range of prior observation. Thus, models of this type are generally not suited for predicting the fate of new chemicals and are not considered in these guidelines.

The theoretical approach is based upon an understanding of environmental fate and transport processes including biotransformation, hydrolysis, oxidation, photolysis, ionization, sorption, volatilization, bioconcentration, and physical transport. This type of model is considerably more versatile since it is designed to predict environmental fate and pollutant concentrations based upon degradation rate constants and relatively simple chemical and environmental input data. Therefore, theoretical models can be applied to chemicals which haven't yet been introduced into the environment. Such models are of considerable interest to the U.S. Environmental Protection Agency and in particular, the OPTS.

The guidance provided is organized into sections with the first addressing steps in the validation process while subsequent sections cover the environmental fate processes and field methods for collecting environmental input and output data. The major steps in the validation process are outlined in Table 1-1 and are discussed at length in the first section of this report.

Much of the information presented relates to the identification of potential problems associated with field validation of models. Validation of a model is defined in this report as comparison of model results with numerical data derived from observations of the environment. Complete model validation requires testing over the full range of conditions for which predictions are intended. At a minimum, this requires a series of validations in various aquatic environments (streams, lakes, estuaries) with chemicals that typify the major fate and transport processes. Where possible, suggested solutions or approaches have been presented but many problems are specific to a particular site, compound, or model and will have to be dealt with on a case-by-case basis. In addition, a model development and subsequent validation is a dynamic process by its very nature. Future research regarding fate and transport processes will refine fundamental theory. This information can then be used to improve existing models. As models are updated, the methods to measure model inputs and outputs must be changed to reflect model improvements.

Sections describing fate and transport processes include the following information: a general description of the process, a list and discussion of environmental factors affecting the process, a list of the priority organic pollutants for which the process is important, a list of model specific environmental inputs and finally, field methods for collecting these input data. The report also briefly covers the collection of input loading data, field sampling for predicted model outputs, and quality assurance. Experience gained during field validations of the EXAMS model (Pollard et al., 1983, Hern et al., in press) was used to modify and improve this document. The guidance provided by this document was constructed for simplified aquatic fate and transport models, e.g. EXAMS. However, the steps in field validation and many of the environmental measurement techniques would apply to all aquatic fate and transport models.

TABLE 1-1. STEPS IN FIELD VALIDATION OF AQUATIC FATE AND TRANSPORT MODELS

Step 1. Identify Model User's Need: The first step in field validation is to obtain a clear understanding of the model user's need i.e., how will the model be used.

Step 2. Develop Acceptance Criteria for Validations: The model user must provide criteria against which the model is to be judged.

Step 3. Examine the Model: This step involves a detailed examination of the model to precisely define input data requirements, output predictions and model assumptions.

Step 4. Evaluate the Feasibility of Field Validation: Some models can not be validated in the field and the validator should consider this possibility.

Step 5. Determine Field Validation Scenario: Many different approaches to field validation are possible. A scenario should be identified and approved by the model user.

Step 6. Plan and Conduct Field Validations Which Should Include the Following Steps:

  Step 6a. Select a Site and Compound(s): There are many important factors to consider in selecting a site and compound(s).

  Step 6b. Collect Preliminary Data and Performance of Sensitivity Analysis: Preliminary data are required to conduct a sensitivity analysis and determine the most important input variables.

(continued)

TABLE 1-1. (Continued)

| | |
|---|---|
| Step 6c. | Develop a Field Study Design: Development of a detailed field sampling plan for the specific model compound and site. |
| Step 6d. | Conduct Field Study: Implementation of the field plan is not addressed in these guidelines. |
| Step 6e. | Analyze Samples: Many analytical procedures are available depending on the chemical and the matrix. Validated methods should be used together with a sound quality assurance program. Selected references for analytical methods are presented in the Sample Collection, Handling and Analysis section. |
| Step 6f. | Compare Model Performance with Acceptance Criteria: A comparison must be made between the model's performance and the user's acceptance criteria. |

## STEPS IN THE FIELD VALIDATION OF AQUATIC FATE AND TRANSPORT MODELS

### STEP 1: IDENTIFY MODEL USER'S NEED

The first step in model validation is to obtain a detailed understanding of the problem confronting a potential model user. This understanding should be acquired through direct discussion with the user. The model validator should elicit from the user how the model will be used, what model input data will be available, how such data will be acquired, and what the expected model outputs are (Donigian 1980).

This problem identification step is important because a valid model is one which is capable of meeting the user's needs. Thus, it is essential to have a thorough understanding of the problem to make an assessment regarding the model's utility. If the model is to be used in several ways or for several different purposes, each use or purpose needs to be defined at the outset. Just because a model has been found valid for one use does not mean it is valid for some other use. The validator may discover, after a detailed review of the model, that the model cannot be used as proposed because of the model's assumptions, the cost of obtaining the input data, etc., and thus save the user considerable time and expense involved in attempting a field validation.

### STEP 2: DEVELOP ACCEPTANCE CRITERIA FOR VALIDATIONS

Prior to attempting to validate a model, the user should develop and provide to the validator the criteria that will be used to accept or reject the model. After identifying the problem and determining how the model may assist in resolving the problem, the user should have a good idea as to the accuracy and precision required of the model. In developing acceptance criteria, the user should consider the predictive ability of alternate methods available to solve the problem, e.g., a model ecosystem. The development of such criteria, however, should not result in either automatic acceptance if the criteria are met or automatic rejection if the criteria are not met (Davis 1980).

The acceptance criteria for a validation should be given in terms of required accuracy, precision and confidence interval. An example of acceptance criteria is as follows: a user wants to estimate the level of some pollutant in sediment within ± one order of magnitude and be correct 95 percent of the time. On the other hand, the criteria for the level of a pollutant in water may be ± 100 percent with the same confidence level since water is of greater concern to the user.

Consideration should be given to the uncertainty associated with model predictions. Knowledge of the confidence interval associated with model predictions "is of considerable practical and theoretical importance, permitting quantitative comparison of model ouput and validation data, clearly indicating the resolution or precision of the model prediction, and placing model predictions in the proper context" (O'Neill and Gardner 1979). Ideally, the user's desired confidence interval about the model's predictions will fall within the accuracy acceptance interval about the field data.

Lack of acceptance criteria could result in attempts to validate a model that could not possibly satisfy the user. It may be appropriate to reject a model prior to any field testing after considering the effect of input sampling errors on the model's predictions. For example, sensitivity analyses might indicate that the input rate constants would have to be determined an infeasible number of times to achieve satisfactory confidence in the output estimates.

## STEP 3: EXAMINE THE MODEL

This examination should concentrate on determining the required inputs to the model (chemical, biological, and physical), the predictions made by the model and the assumptions made in the construction of the model. A model input should be determined only for each environmental fate process by which the compound of interest degrades, e.g., photolysis, hydrolysis, etc.

In examining model inputs, it is important to precisely define each input and determine the units of measure. For example, "suspended particulate" might be defined to include particulate organic matter or only inorganics and the units could be mg/l dry, wet, or ash free dry weight. Other considerations include determining whether a model's input values should represent an average for some compartment or box, an average from some river or lake cross-section, etc., and whether these averages represent one point in time or some length of time. It is essential to precisely identify all model inputs to ensure a fair test of the model.

Model outputs must also be carefully defined. A prediction of x ppm in water could refer to whole water including organic and inorganic particulate matter or it might mean filtered or centrifuged water. A pollutant concentration in fish may be based upon whole body wet weight, whole body dry weight, edible portion only, etc.

The final major considerations in model examination are the assumptions upon which the model is based. Assumptions are frequently made to simplify a model and this usually restricts the situations to which it is applicable. Some model assumptions are considerably more important than others and attempts are frequently made to verify a model under conditions that violate some of its assumptions. However, serious violation of an assumption will likely result in an invalid test of the model. A more detailed discussion of model assumptions and designing around them is found in the section on Development of a Field Plan.

## STEP 4: EVALUATE THE FEASIBILITY OF FIELD VALIDATION

Field validation is probably the most credible test of a model but not all models should be field tested. Some of the reasons that a model cannot be validated relate to model assumptions, the inability to provide input data, the inability to quantify model outputs in the field, and large sampling errors associated with model inputs. The model validator has an obligation to determine whether field validation should be attempted. The results of such inappropriate testing can have a significant impact upon the use and credibility of a model even if the tests were poorly designed and implemented.

The foregoing is not intended to imply that field validation should not be attempted, only that caution and judgment should be exercised. There are means to design around some model assumptions, indirectly collecting some input and output data and improving model precision. The following are examples of instances where the feasibility of field validation may be questioned.

- A model that assumes steady state or a dynamic equilibrium may be difficult to field validate fully. Steady state conditions do not exist for long in the environment; temperature, flow rates, pollutant loads, bacteria population, etc., are almost always changing. Steady state may be approximated for brief periods in rivers but it may be impossible to achieve such conditions for compounds that have long half-lives.

- In some models, input data may not be quantifiable. Examples of such inputs are the active pollutant degrading fraction of the total bacteria population and the molar concentration of oxidants in water that are capable of causing induced photolysis. No standard or routine procedure exists for directly acquiring these data although it is sometimes possible to obtain such data indirectly.

- As an example of uncollectable output data, consider a model that predicts the concentrations of organic pollutants on clay. Currently, no methods exist for separating clay from sand and silt without affecting the concentration of volatile or semi-volatile organic compounds.

- An example where it would be infeasible to field test a model due to a large input sampling error is as follows: assume a degradation rate constant is measured several times and the results vary by orders of magnitude. If this input is sensitive in the model (a small change in the input results in a large change in the output) the resultant prediction will also have a very large sampling error; probably much greater than the user's acceptance criteria for precision.

In summary, it is important to realize that field validation is not always practical. Persons involved in possible field tests must make this determination on a case-by-case basis.

## STEP 5: DETERMINE FIELD VALIDATION SCENARIO

There are many possible field validation scenarios that could be proposed. Below, three possible scenarios are considered and the various attributes and limitations of each are discussed. The selection of a scenario for attempting to validate a model should be made by the model user. The basis of the decision will involve consideration of the degree of credibility required, the feasibility of field testing all environmental processes considered by the model, the length of time available for testing, environmental impacts, and finally, costs. The scenarios to be discussed are: 1) laboratory testing supported by field validations; 2) controlled field validation; and 3) uncontrolled field validation.

### Laboratory Testing Supported By Field Validations

This approach involves extensive testing of a model and each of its processes in controlled environments followed by a few field tests using compounds which undergo several environmental processes. The controlled environments may be fairly simple laboratory microcosms or complex artificial streams such as the ones at the EPA's Environmental Research Laboratory at Athens, Georgia. Such systems offer a relatively high degree of environmental control with varying degrees of complexity and "real world" simulation.

They also permit detailed study of processes at relatively low expense, and can avoid some problems associated with model assumptions. The limitations of the scenario are that the results of tests in artificial environments lack credibility since artificial environments only approximate the "real world," and limited field testing may not detect significant model deficiencies resulting from extrapolation of laboratory studies to the field. A few field tests on compounds with complex environmental fate do not adequately test each process in the model but would add to the credibility of the laboratory tests.

### Controlled Field Validation

Controlled field validation, as envisioned here, entails dosing natural or seminatural aquatic systems with selected compounds to test each environmental fate process. Each process in the model is actually a sub-model and needs to be tested separately. It is entirely possible for the model of one process to be in error while all other processes are acceptably accurate.

An environment versus process matrix (Figure 1-1) should be developed and the required validations conducted. Many of the tests required to complete such a matrix could be conducted in a single study. For example, a small pond might be dosed with low levels of relatively non-toxic compounds with each typifying one of the following environmental processes: oxidation, hydrolysis, photolysis, biotransformations, ionization, volatilization, sorption, bioconcentration, and physical transport. Thus, if all compounds were added to a single pond, all the processes of the model pertaining to such an environment could be simultaneously tested. Similar studies would, of course, have to be conducted on other types of aquatic environments. A few such studies could yield very credible tests in natural ecosystems at a relatively economical cost compared with uncontrolled field validation. Controlled testing of this type necessitates the addition of contaminants to aquatic systems. This may be scientifically justifiable and environmentally acceptable, yet politically impossible. There are, however, several ways to avoid or minimize problems associated with intentional dosing. Isolated locations might be used to avoid exposure to the public or the effluent from a dosed pond could be cleaned up. An example of the latter is the seminatural stream currently being used at EPA's Monticello, Minnesota laboratory. Natural river water is dosed, run through an artificial stream bed and the water is treated before it is discharged (under permit) back to the river.

| | Biotransformation | Photolysis | Oxidation | Hydrolysis | Ionization | Sorption | Volatization | Bioaccumulation | Physical Transport |
|---|---|---|---|---|---|---|---|---|---|
| **Turbid River** | | | | | | | | | |
| **Stream** | | | | | | | | | |
| **Pond** | | | | | | | | | |
| **Oligotrohic Lake** | | | | | | | | | |
| **Eutrophic Lake** | | | | | | | | | |
| **Estuary** | | | | | | | | | |

Figure 1-1. Field validation matrix.

Many of the environmental hazards associated with working with priority pollutants can be avoided by using deuterium labeled natural water components or relatively nontoxic compounds, e.g., ethanol could be used to test biotransformation instead of the priority pollutant, phenol. In summary, the controlled field approach is a relatively inexpensive approach to obtain credible field data but it may entail some political considerations.

### Uncontrolled Field Validation

Uncontrolled field validation involves attempting to test each process of an aquatic fate and transport model using natural water bodies and uncontrolled (by the validator) contaminant loading. Such sites might be a river, lake or pond receiving contaminant loads from direct industrial discharge, non-point sources (urban and agricultural runoff), atmospheric deposition, contaminated ground water infiltration, municipal waste water discharges, other surface water flows, etc. The main advantage of field validation using this scenario is one of credibility. Having validated a model under "real world" conditions is frequently regarded as the ultimate test of a model. The more complex the test with multiple sources of various types, the more credible is the test. However, such increased complexity generally adds to the cost of testing, increases the sources of errors, may result in compensating errors, makes data interpretation more difficult, and yields less precise predictions.

This approach to model validation should be based on the same matrix of validation tests as described in the previous scenario (Figure 1-1). Field validation using this matrix consists of a series of tests using selected sites and compounds that typify each environment and process. A model that meets the user's acceptance criteria for each test in the matrix would then be considered valid. The number of replications for each box in the matrix depends upon the level of confidence desired by the user as well as the resources available. This approach requires a large number of field tests to fill in the matrix. Therefore, it would probably only be possible to test a few processes at any one site. This method then becomes very resource intensive.

Another consideration in this scenario is the selection of validation sites. Most of the organic chemical discharge data pertains to the priority pollutants. Because of EPA's interest in these pollutants and their potential adverse effects, efforts are being made to minimize their release. This results in low pollutant levels in effluents and frequently undetectable levels in receiving waters.

## STEP 6: PLAN AND CONDUCT FIELD VALIDATIONS

This section addresses the design of field studies to test a process type aquatic fate and transport model. At this stage the model has been examined and all required environmental and chemical inputs identified by process. The outputs of the model are known and all the assumptions and design limitations thoroughly understood. The model has been judged potentially capable of meeting the user's needs, the user's acceptance criteria have been established, and a preliminary decision has been made that field validation is feasible. Finally, a validation strategy has been identified in consultation with the model user.

With these important preliminaries completed, the design of a field validation study can begin. The steps in this process include site and compound selection, collection of preliminary data sets, a sensitivity evaluation, development of a field plan and its implementation, analysis of samples, and comparison of model performance with acceptance criteria.

### STEP 6a: Select Site and Compound(s)

Site and compound selection must be considered together. It is most likely that not all the selection criteria can be met at any one location and the importance of each factor must be weighed by the investigator.

### Compound-Selection Factors

Analytical Methods--

Methods must exist for quantifying the input loadings to the model and for determining the concentration of the compound of interest in the environmental media (water, sediment, biota, etc.) considered by the model. The EPA has developed standard methods for determining many organic compounds in water but no similar EPA approved procedures exist for sediment and biota. The precision, accuracy and limits of detection also need to be determined for each medium. The detection limits should be reviewed after consideration of the expected levels at a site. A final factor to consider may be the cost of making the determinations.

Compound-Specific Model Inputs--

A well-designed field study is based, in part, upon a sensitivity analysis of the model. Thus, preliminary model runs must be made and these require compound specific inputs such as aqueous solubility, octanol water partitioning coefficients, degradation rate constants, etc. The availability of such input data may be a factor in selecting compounds. Ultimately the precision and accuracy of such inputs are also required. Most rate constants that are available are based on laboratory tests using the neutral species of the test compound. Since little information is available for ionic forms, usually rate constants are assumed to be the same for neutral and ionic species. This assumption may not be valid, depending on the compound under investigation. The validator should be aware of this potential source of error when conductinng field studies.

Environmental Fate--

The environmental fate of the compound is important to the three validation scenarios presented. For the scenario in which a few field validations are conducted to support laboratory tests, compounds that undergo multiple processes should be sought. In the controlled and uncontrolled field validation scenarios, compounds should be selected to typify a single environmental process to the extent possible. In all cases, the predicted half-life of the compound by each process must be considered relative to the time which the compound can be followed (tracking time). For example, a compound that hydrolyzes with a half-life of 7 days would not adequately test a model if that compound could only be followed for 2 days in a river. Ideally, the compound should be tracked through several half-lives. The compound-specific model inputs and canonical environments can be run in the model to estimate environmental fate.

Compound Toxicity and Environmental Hazard--

This factor is usually only significant when a compound or compounds are being added to a natural water body (scenario 2). If this approach is pursued and a suitable site is located, the least toxic compounds representative of a process should be selected. The priority pollutants are obviously undesirable contaminants, but there are many readily degradable organic compounds that could be added to a water body, traced through several half-lives and pose no significant threat to the environment. For example, some dyes used as water tracers are easily photolyzed and therefore might be used to test that process. Other dyes such as rhodamine B might be used to examine sediment transport and sorption.

Contaminant Source--

In controlled field validation, the selection of a pollutant source is obviously no problem since the investigator actually doses the water body. For the other two scenarios, the investigator is restricted to selecting compounds that already exist in concentrations that can be tracked in aquatic systems. Although many compounds have been detected in effluents, relatively few have been found in easily detectable concentrations in the receiving waters.

## Site Selection Factors

### Traceable Level of Compounds--

The key factor in site selection is that the compound of interest must be present at sufficiently high levels so that it can be traced for a considerable distance or time period. This translates to being able to follow a compound through several half-lives for processes involving degradation or volatilization. For sorption, physical transport and bioconcentration, it means detecting the compound of interest in various media at significant distance/time from the source. Factors influencing traceability include the input load, water body size, flow rate, transformation half-life of the compound, mixing, and dilution by other water inputs such as merging streams.

### Ability to Collect Site Specific Input Data--

The collection of most site specific model input data presents no unusual problems; however, the required inputs should be reviewed to assure this. Particular consideration should be given to mixing, flow, sediment transport, ground water infiltration, and fish movement. Weather, season of the year, size of water body, site access, and many other factors can also affect the feasibility of collecting data.

### Historical Data on Site Specific Model Inputs--

If historical data are available, they can be used to conduct preliminary model runs and sensitivity analyses. Depending upon the amount and type of data available, it may not be necessary to conduct a preliminary sampling study.

### Quantifiable Input Loadings--

The pollutant load to the aquatic system must be known to adequately test the model. The accuracy of these data will depend upon the types and number of sources, their relative loading, and their variability. A single, steady state point source is probably the simplest situation while nonpoint sources, contaminated ground water infiltration, and atmospheric deposition add significant complexity. The additional complexity can result in a less definitive test of a model. For example, if a nonpoint source (NPS) model is used to predict loadings, the accuracy and precision of the model's estimate must be considered. If the output of the NPS model is in error, the output of the aquatic fate and transport model will also be in error. Input loading models should be tested and validated separately from aquatic fate and transport models.

It is recommended that sites with easily quantified inputs be used to verify in-stream processes. Multiple sources may significantly increase the expense of collecting data, increase input errors, and complicate data interpretation. Theoretically, if the model is capable of predicting the pollutant concentrations from one source with distance or time, it should be capable of doing so for multiple sources.

Site Related Analytical Problems--

Chemicals found in industrial effluents, or in the water body to be studied, may interfere with analyzing for the compound(s) of interest. Samples of effluents, water, and other media of interest should be analyzed prior to any major field study. If interferences are found, sample cleanup procedures must be developed prior to further sampling efforts.

Model Assumptions Relative to Site--

In selecting a site, it is necessary to review the assumptions made in developing the model. Specific assumptions such as complete mixing, steady state, lack of toxic effect, etc., are discussed in the section on development of a field plan. Basically, conditions at the site should not seriously violate assumptions of the model. Proper site and compound selection also offer an opportunity to design around some model assumptions.

Water Body Type and Validation Scenario--

The site for the field validation must fit into the validation plan, i.e., the matrix approach discussed under the controlled and uncontrolled field validation scenarios. The selection of a water body type should be done in conjunction with the compound selection. Compounds with short or long half-lives can easily be studied in small, well-mixed ponds. Large lakes can also be used, but defining horizontal and vertical mixing can pose problems with point source loadings such as from rivers and effluents. Rivers and streams are best suited for testing the degradation or volatilization process of short-lived compounds. Generally long-lived compounds should only be used to test physical transport and bioaccumulation processes. It is usually impossible to track long-lived compounds through several half-lives in rivers and streams.

Overall Site Simplicity--

Generally, the simpler the site in terms of the amount of data that must be obtained, the more cost effective the validation effort. The site should, of course, be chosen wisely and must result in a sufficient test of the model. Multiple sources, many major dilutions, and significant environmental changes from compartment to compartment (for box-type models) add greatly to the costs and difficulty of field validating a model. Greater complexity usually results in more sources of error which result in a wider confidence interval about predicted values.

## Approaches to Selecting Compounds and Sites

The approach to compound and site selection depends upon the validation scenario selected (i.e., laboratory, controlled field, or uncontrolled field). Some compounds degrade via multiple fate processes while others degrade by a single process. Sites for field validations may cover the spectrum from specially constructed environments and small research ponds, streams, and lagoons to large natural rivers, lakes, and estuaries.

The selection of a chemical for study depends greatly upon its fate in aquatic environments. Data on the "Water Related Environmental Fate of 129 Priority Pollutants" were assembled and published by EPA (Callahan et al. 1979). Additional information on 114 of these has been assembled in a form useful to the EXAMS model and released in a final draft report titled "Aquatic Fate Process Data for Organic Priority Pollutants" (Mabey et al. 1982). In addition, fairly complete data exist on the compounds which were studied during the development of the SRI model (Smith et al. 1978): p-cresol, benz(a)anthracene, benzo(a)pyrene, quinoline, benzo(f)quinoline, 9H-carbazole, 7H-dibenzo(c,g)carbazole, benzo(b)thiophene, dibenzothiophene, methyl parathion, and mirex. Probably the next most studied organic compounds are the pesticides, but it is beyond the scope of these guidelines to provide information or references.

Perhaps the most direct and obvious method of finding a study site is to consult with persons engaged in model development and testing. Other sources of information are the Surveillance and Analysis Divisions of EPA's Regional offices, and State and local water pollution control personnel. These people may know of sites that meet some or most of the site selection criteria. In locating sites where contaminants can be added to a water body, various government owned reservations, government sponsored national laboratories, private research contractors, and organizations equipped with semi-natural streams, ponds, etc. should be contacted.

Several computerized data bases exist which may be helpful in site selection. The STORET (STOrage and RETrieval) data base (Taylor 1980) contains information relating to the quality of waterways within and contiguous to the United States. Data from a geographic area around a site may be obtained or information on sites where specific compounds have been found can also be sought. For information and assistance, contact STORET User Assistance in Washington, D.C., (202) 426-7792. The Industrial Facility Discharge (IFD) file may also be useful. It contains data on individual facilities and can be searched by type of industry. The Reach File is a data system organized by hydrologic structure and is used for organizing water resources and environmental data, including the waste water discharge information and the IFD file. Final manuals on both the Reach File and the IFD file are being prepared. For information and assistance, contact the Office of Water Regulations and Standards (WH-553) U.S. Environmental Protection Agency, Washington, D.C. 20460.

## STEP 6b: Collect Preliminary Data and Conduct Sensitivity Analysis

### Sensitivity

Sensitivity of a model to an input is the rate of change of the model's output caused by a change in that input. If a change in an input causes a large change in the output, the model is sensitive to that input; or if a change in an input causes a small change in the output, the model is insensitive to that input. A sensitivity analysis identifies which inputs have a large influence on output and need more input accuracy and precision. Using model sensitivities to plan the sampling design and to choose the number of samples can aid in obtaining the appropriate accuracy and precision for the model users needs. The similarity of model sensitivities to the sensitivity of the real system is tentatively assumed in designing the initial sensitivity study and must be proven for validation.

There are stochastic techniques for determining the mathematical sensitivity of input parameters which are based upon Monte Carlo simulation (Hoffman and Gardner 1983). These techniques are relatively complex and could be quite tedious to perform with a model such as EXAMS which often requires numerous input parameters. Mathematical sensitivity analysis becomes increasingly untenable as the number of input parameters to be varied by the model user increases. Therefore, this type of sensitivity analysis is generally inappropriate for the purposes of determining sampling effort distribution unless the Monte Carlo simulation is built into the model.

Hoffman and Gardner (in press) present a technique for sensitivity screening using a simple sensitivity index. This index can be easily calculated with estimates of input parameter values, and input parameters variability. Best estimates of input parameters and their associated variability (standard deviations, ranges, etc.) can be obtained during preliminary surveys or from the literature. The index is then calculated as follows:

$$S = 1 - (C_{min}/C_{max})$$

where: $S$ = relative sensitivity

$C_{min}$ = low model output concentration based on one extreme input parameter estimate

$C_{max}$ = high model output concentration based on the other extreme input parameter estimate.

The index will vary between zero and one with zero representing unused parameters and one representing hypersensitive parameters. Indices can be calculated for all input parameters necessary for the model to simulate a given compound's fate and transport. These indices can then be ranked according to magnitude and decisions regarding distribution of sampling effort made. These decisions should take into account the relative sensitivity of input parameters, the accuracy and precision required by the model user, and the funding available for the field validation.

The amount of information necessary for best estimates of input parameters may be quite different depending upon the sensitivity of the parameter. It is possible for a given input parameter to be hypersensitive under one set of environmental conditions and insensitive under another set of conditions. This can be best illustrated using a simple example of a compound that degrades primarily by acid/base hydrolysis. For purposes of this example, a hydrolysis-sensitive compound was entered into EXAMS data base and model outputs generated by varying the pH between 5 and 9 while holding all other inputs constant. Sensitivity indices were calculated for various ranges of pH using the methods presented above. EXAMS concentrations from ten hours after dosing were used in the calculations since compound levels were simulated as being detectable for all pH levels at this simulation time. Since pH is known to be an important input parameter for hydrolytic degradation (Burns et al. 1982), relative sensitivities should have reflected this by indicating pH as a hypersensitive parameter. With our test compound example, this was not always the case. In fact, acid/base hydrolytic sensitivities to pH varied from 0.0 to 0.99 depending on the range of pH entered into the calculation (Table 1-2).

TABLE 1-2. EXAMS CONCENTRATION OUTPUT AND RELATIVE SENSITIVITY OF pH INPUT FOR A COMPOUND WHICH DEGRADES PRIMARILY VIA ACID/BASE HYDROLYSIS

| Combinations of Parameter Ranges | EXAMS Output $C_{min}/C_{max}$ | Calculated Relative Sensitivity |
|---|---|---|
| pH 5/9 | 27/27 | 0 |
| pH 5/8 | 27/1700 | 0.98 |
| pH 5/7 | 27/2470 | 0.99 |
| pH 5/6 | 27/1700 | 0.98 |
| pH 6/9 | 27/1700 | 0.98 |
| pH 6/8 | 1700/1700 | 0 |
| pH 6/7 | 1700/2470 | 0.31 |
| pH 7/9 | 27/2470 | 0.99 |
| pH 7/8 | 1700/2470 | 0.31 |
| pH 8/9 | 27/1700 | 0.98 |

This example points out a potential problem in use of this sensitivity index. For parameters of this type it is necessary to have very good estimates of the range of environmental conditions to be encountered during a validation attempt. In this case an underestimate or overestimate of the range of pH expected to be encountered during the study could have provided a gross underestimate of the sensitivity of this parameter. This would have, in turn, provided an erroneous basis for decisions regarding distribution of sampling effort. Parameters of this sort can be identified by calculating sensitivities at various input parameter levels and checking the results for anomalous values of the sensitivity index over-increased ranges of the input parameter values. Once hypersensitive parameters or hypersensitive/insensitive parameters have been identified, appropriate effort can be expended to define the range of expected environmental variability prior to the validation attempt.

Relative parameter sensitivity may become a very important consideration for parameters which undergo significant degradation via other process pathways as environmental conditions change. For example, if the compound used in the above example underwent moderate biotransformation within the pH range of 5 to 9, but was only hydrolyzed rapidly above pH 8 or below pH 6, it would be very important to know the precise value of the expected pH as well as the range of pH fluctuations.

In summary, calculation of simple sensitivity indices based on the response of model output to changes in model input parameters can aid in making decisions regarding the amount of sampling effort to be expended for various model input parameters. In addition, input parameters whose sensitivities change as environmental conditions change can be identified using this simple index. Decisions regarding distribution of sampling effort among various input parameters can then be facilitated based upon the relative magnitudes of the calculated sensitivity indices.

### STEP 6c: Develop a Field Study Design

In designing a field study one must consider the compound, site, required input and output data, model assumptions, other possible design complications, results of the sensitivity analysis, safety aspects, and the appropriate statistical design. Once the compound and site are selected the sensitivity analysis (see previous section) will help define the appropriate samples to be collected, sample size, and the statistical design. Table 1-3 presents a list of topics related to the selected compound and site which must be addressed or considered in the preparation of a field protocol.

TABLE 1-3. CHECKLIST FOR FIELD PROTOCOL PREPARATION

A. DESIGN CONSIDERATIONS

1. Validation scenario satisfied - Selected site (type) and compound (degradation routes) meet requirements of validation scenario
2. Rate constant information available
3. Model assumptions satisfied
4. Sample type required - Water, sediment, pH, etc.
5. Number of samples of each type required
6. Time and/or distance compound can be detected
7. Location where samples are collected - Time and/or space
8. Quality assurance - Field and laboratory replicates, knowns, splits, blanks, etc.
9. Statistical design - Comparison of predicted and observed estimates with validation criteria

(continued)

TABLE 1-3. (Continued)

B. OTHER ELEMENTS OF THE FIELD PROTOCOL

1. Sample Collection
   a. Sampling procedures
   b. Sample collection gear - Pumps, dredges, nets, etc.
   c. Sample containers - Glass jars, teflon bottles, etc.
   d. Sample container preparation - Soap and water wash, etc.
   e. Sample preservation - $H_2SO_4$, NaOH, $HgCl_2$, etc.
   f. Sample coding
   g. Shipment of samples to laboratory
2. Chemical Analysis - Methods for each compound and media
   a. Detection limits
   b. Proper sample size - Volume or mass
   c. Matrix problems - Sediment, biological, etc.
3. Logistics
   a. Schedules
   b. Record keeping - Field notebooks, data forms, etc.
   c. Vehicles - Cars, trucks, boats, etc.
   d. Maps
   e. Access - Permission to sample effluents, boat ramps, etc.
   f. Notification of local, state, and federal authorities
   g. Personnel - Competent team leader, reliable assistants
   h. Data management - How data will be massaged, reduced, etc.
4. Safety Aspects - Proper handling procedures, emergency procedures

## Validation Scenario

The site and compound(s) selected should be an integral and supportive component of any validation scenario. In the first scenario, a few field tests would be conducted on compounds of complex environmental fate to add credibility to laboratory tests. In contrast, the field test in validation scenario three, would be conducted with a compound of simple environmental fate and a specific environmental type. Therefore, it is important to ask the question, does the site and compound(s) selected support the overall objectives of the chosen validation scenario?

## Rate Constant Information

It is essential to have reliable rate constant information to conduct a field validation study. In most fate and transport models, rate constants are coupled with site specific environmental parameters to produce site specific rates. Conceptually the rate constants are the main determinant of the fate of a compound which is only modified by environmental data. Often, an investigator is faced with undesirable situations with regard to rate constants:

1. Several rate constants are obtainable from the literature for a very sensitive process but the rates vary over several orders of magnitude. Since this input is sensitive in the model the resultant prediction will also have a very large sampling error. If the sampling error is much greater than the user's acceptance criteria for precision it would be infeasible to field test the model.

2. Only one rate constant with no estimate of its variance can be obtained from the literature for a given sensitive process. In this case, one cannot determine confidence limits for the model's predictions.

If rate constants do not exist, an investigator may be forced to develop this information or select another compound. Methods to determine rate constants do exist, e.g., SRI International has developed laboratory protocols for determining aquatic rate constants for hydrolysis, photolysis, oxidation, biodegradation, volatilization and sorption (Mill et al. 1982). Rate constants are available from a variety of sources. Two excellent sources available in the literature are Mabey et al. (1982) and Lyman et al. (1982).

## Model Assumptions

After the model examination step has been completed, the model's inputs, outputs, and assumptions will be carefully detailed. The assumptions associated with any fate and transport model must be met to conduct a totally valid field test. Table 1-4 lists assumptions commonly used in aquatic fate and transport models.

Theoretically, it is pointless to conduct a field validation study if any one of the model's assumptions is violated. Few, if any, field validation studies could be conducted if an investigator had to strictly comply with all of a given model's assumptions. However, an investigator may simulate compliance of a model's assumptions. For example, most models assume that a compartment is a completely mixed (homogeneous) box where a single parameter value represents conditions throughout the entire compartment. An investigator may simulate compliance by using average values which are representive of the true compartment mean values.

TABLE 1-4. ASSUMPTIONS COMMONLY ASSOCIATED WITH COMPARTMENTALIZED AQUATIC FATE AND TRANSPORT MODELS

1. Steady state - Loading, water flows, bedload movement constant within a given compartment over time.
2. Homogeneous compartments - A compartment is completely homogeneous (completely mixed) with respect to all parameters. Therefore, only a single value is required to represent a given compartment parameter.
3. Pollutant levels will not change pseudo-first order kinetics - (a) no direct toxic effects on biota, and (b) no interaction between organic pollutants, i.e., no synergistic or antagonistic reactions.
4. Sorption and ionization are essentially instantaneous processes within each compartment, i.e., much faster than physical transport or transformations.
5. Subroutines which use rate constants and site specific environmental parameters actually account for the variation of transport and fate phenomenon. Standard plate counts represent total bacterial populations or organic carbon contents of sediments can be used to "normalize" sorption coefficients for neutral hydrophobic organics.
6. Mass balance - The mass of the loadings equals the mass of the degradation products and/or mass of the transport products.
7. Environmental variables exist within "normal" ranges - Extreme high temperatures do not lower bacterial degradation rates, water never freezes, etc.

Steady State--

The assumption of steady state (conditions are constant) is a difficult assumption to meet. Many possible field testing situations will be eliminated because of this assumption. Effluents, stream flows, environmental conditions, and bedload movement do vary over time. If a true steady state situation was discovered, a single set of samples, collected without regard for time (e.g., samples collected on a single given day), would be sufficient to verify a model.

Fortunately, conditions do not have to be constant over time ad infinitum, they only need to be constant long enough for an equilibrium to be established between the pollutant and its surrounding environment and long enough to allow one to collect the necessary data on input and output variables. This alone represents a strong rationale for the use of controlled situations, i.e., the second validation scenario.

In addition, input and output parameters can be time-weighted averages that can be used in model validation. However, this is not the ultimate solution to all steady state problems. If equilibrium conditions are reached in days, the time-weighted averages need only to reflect days; however, if equilibrium conditions are not reached for weeks or months, then the time-weighted averages must truly reflect these extended periods.

Steady State Loadings--Industrial effluents or other sources of pollutant loads (model loadings) are rarely constant in pollutant concentration or flow over extended periods of time. However, with an appropriate field plan one may simulate compliance with the steady state loading assumption. For example, an investigator may select a compound and site with the following characteristics:

1. The compound does not sorb to any appreciable extent, (because a pollutant normally reaches equilibrium with water faster than with bottom sediments);

2. the compound obtains equilibrium with its surrounding environment in a relatively short time, i.e., hours;

3. the receiving water, e.g., stream, demonstrates "plug" flow; and

4. the compound has a short half-life relative to tracking time.

Then the investigator can:

1. Establish a "window" of known concentration in the effluent for a short period of time. This could be accomplished by collecting a number of continuously pumped samples to estimate pollutant concentration in the effluent (Figure 1-2). During each 30-minute sampling period a sample would be collected using a peristaltic pump equipped with chemically inert tubing.

2. Mark the known effluent "window" by adding rhodamine WT dye at the mid-point of the effluent monitoring period. The amount of dye needed to mark a certain section of stream and still be detectable a given distance downstream can be determined by methods presented in Kilpatrick (1970).

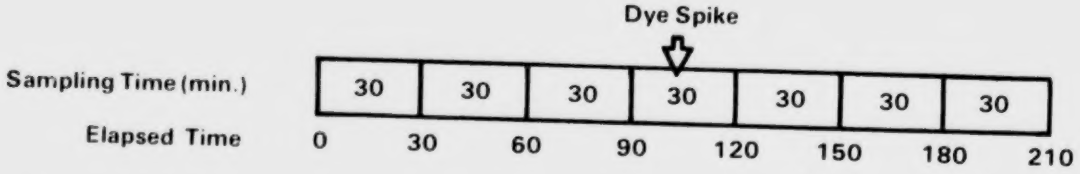

Dye Spike
Sampling Time (min.)
30
30
30
30
30
30
30
Elapsed Time
0
30
60
90
120
150
180
210

Figure 1-2. Effluent sampling.

If no concentration change is detected during the 3 1/2 hour effluent sampling period, a known section of the stream will be contaminated with a known amount of pollutant. Repeated cross-sectional sampling of the center of this water mass (area of maximum dye concentration determined with a portable fluorometer) would permit the pollutant decay curve to be determined. By sampling within the marked water mass at the point of maximum dye concentration, the investigator has simulated compliance with the steady state loading assumption.

Also, another variation on the same theme can be employed by an investigator to simulate compliance with the assumption of steady state loadings. In this case the investigator would mark a section of a stream with rhodamine WT dye and establish a window of known pollutant concentration in the stream itself rather than the effluents to estimate pollutant load (Figure 1-3). Depth-integrated cross-sectional samples would be collected to establish a "window" of known, and hopefully equal, pollutant concentration. This water mass would then be marked at its mid-point with rhodamine WT dye by releasing the dye at a constant rate as the investigator transverses the stream. Repeated cross-sectional sampling of the water mass as it moves downstream would allow the investigator to determine the pollutant decay curve. Also, the problems associated with multiple discharges can be circumvented in this manner. Obviously, the criteria listed above for the site and compound would still apply.

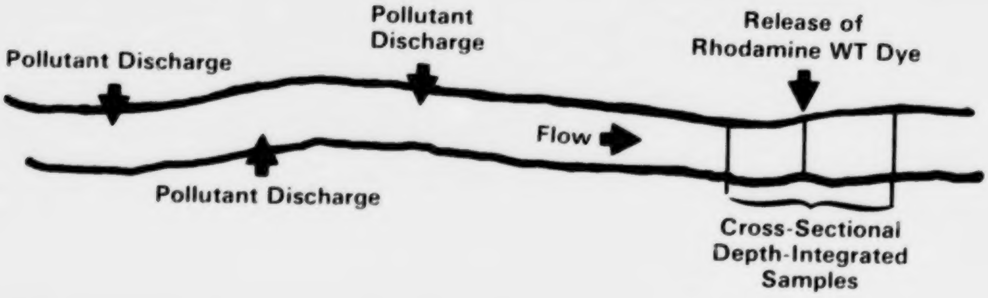

Pollutant Discharge
Pollutant Discharge
Release of Rhodamine WT Dye
Flow
Pollutant Discharge
Cross-Sectional Depth-Integrated Samples

Figure 1-3. Simulating compliance of steady state loading.

Steady State Flows--An investigator may find the following suggestions useful in simulating compliance with the assumption of steady state flows:

1. Select a site where flows are relatively stable, e.g., downstream from a flow regulation dam,
2. Select time of year when flows are relatively stable--often summer,
3. Use controlled situations,
4. Use dye as discussed previously, or,
5. Use a pond or lake where short-term flow changes have little effect on lake or pond volume.

Steady State Bedload Movement--Bedload movement is difficult to measure and often erratic. A high percentage of the yearly bedload movement will often occur in a short period of time in a given stream, e.g., after rainstorms, floods, snow melt, etc. Therefore, a single set of sediment samples often will not accurately reflect steady state bedload movement. To aid an investigator in simulating compliance with the assumption of steady state bedload movement the following suggestions are offered:

1. Select a site which reduces the probability of bedload movement - lake, pond, or extremely sluggish river,
2. Select a stream which is flow regulated,
3. Use controlled situations - artificial stream, etc.,
4. Select a compound which does not sorb so that bedload movement is not important, or,
5. Select a compound which sorbs but has a relatively short half life. Also, conduct this study where there is a low probability of erratic bedload movement (low flow in stream).

Homogeneous Compartments--

Fate and transport models may assume that a compartment is a completely mixed box (homogeneous) where a single parameter value represents conditions throughout the entire compartment. To simulate compliance with this assumption, an investigator could reduce compartment sizes to reduce compartment variability, and/or use average values obtained from either composite or multiple samples.

Mass Balance--

Models equate the mass of the chemical loading to the mass of the chemical in the output predictions (mass balance). The model's mass balance equations account for removal from the modeled system by transport, changes from one phase to another within the modeled system (e.g., sorption) and losses within the modeled system (e.g., degradation). To account for the chemical mass present within the system it may be necessary to collect suspended material, sediment, interstitial water, and biota, depending on the chemical of interest.

Environmental Variables Exist Within Normal Ranges--

Most fate and transport models' subroutines are set so that extreme environmental conditions (pH value of 1, temperature of 80°C, etc.) will not change pseudo - first order kinetics. Temperature is one of the most important environmental conditions determining degradation rates. The influence of temperature on physiological processes can be measured by a rate called $Q_{10}$. This value is the rate at which processes increase with a 10°C rise in temperature. For biological processes, $Q_{10}$ values generally range from 2 to 3. The principle operates only within the range of tolerance of a given species. However, a model given an ambient temperature of 80°C may increase physiological processes (bacterial degradation rates, bioconcentration) according to the $Q_{10}$ rule even though most organisms would be eliminated.

Normally it would be inappropriate to field test models in extreme environments since the user is generally concerned about the fate and transport of compounds under "normal" environmental conditions. However, if the intended use of the model is for extreme environments (hot spring, acid mine drainage system, etc.) the investigator must take into account the effect of extreme environmental parameter values on the various subroutines.

## Type and Number of Samples

The type of samples to be collected is a function of the model's input requirements, output statements, and the selected test compound and site. Through a detailed examination of the model, an investigator will determine input data requirements by process (oxidation, physical transport etc.), output predictions and model assumptions. By completing the steps of this report through the sensitivity analysis, an investigator will know by which processes the compound of interest will be degraded or be transported by and, therefore, the type of samples required for the field validation study.

The sensitivity analysis step as previously described will determine the relative number of samples of each type to be collected. The relative number of samples is based on a parameter's sensitivity and variability. The relative number of samples to be collected may have to be tempered by cost and time considerations to give the actual sample size.

## Compartmentalization

Compartmentalization refers to the segmentation of model ecosystems into various "completely-mixed" boxes of known volume and interchange. Interchange betwen compartments is simulated via bulk dispersion or equal counterflows between compartments. Compartmentalization is a popular assumption in fate and transport modeling because the completely-mixed assumption reduces the set of partial differential equations (in time and space) to one of ordinary differential equations (in time only). Nevertheless, it is possible to recover some coarse spatial information by introducing the appropriate number of interconnected compartments. To select the appropriate number of compartments for a given field validation attempt, the reader is referred to the Physical Transport section.

## Design Features to Eliminate Other Problems

Besides problems which arise from compliance with model assumptions, other problems can plague a validation study. These problems are often related to the selected site, e.g., multiple sources of effluents. Proper site selection can alleviate many problems associated with collecting all of the necessary data for model validation. For example, is it possible to collect large enough quantities of biota for chemical analyses at the selected site? If the model predicts a certain concentration of pollutant in sediments, can representative sediment samples be readily obtained?

Other collection problems can arise, e.g., the model may predict chemical concentration in suspended sediments and plankton. Mutually exclusive and totally discrete samples of this kind are nearly impossible to collect. In this case, an investigator may estimate concentrations by analyzing unfiltered versus filtered water, analyzing mainly plankton samples collected by plankton nets, and fine sediment samples collected from the upper layers of the bottom sediment. Many problems can arise when hydrologic characteristics of the water body are not well defined prior to the initiation of chemical monitoring. Aquatic dyes (e.g., rodamine WT) have been successfully used to establish hydrologic characteristics of water bodies including travel time, mixing zones downstream from effluents, dilution effects, and pollutant dispersal characteristics over the entire length of the water body anticipated to be monitored (Hubbard et al. 1982, Pendleton 1980, Yotsukura and Cobb 1972). In addition, dyes have been used to track compounds, and to determine volume and discharge rates. Generalized techniques for fluorometric procedures to measure dyes can be found in Wilson (1968).

Field validation of aquatic fate and transport models require the collection and quantification of numerous chemical, physical, and biological parameters over time for model input variables and model output variables. Parameters which display large scale perturbations over time can generate problems in quantification of model input data. For example field validation studies which require standing crop estimates should not be attempted in environments which exhibit large temporal biological perturbations (algal blooms). Table 1-5 lists some common problems and suggests possible solutions.

## Sampling Location

Selection of sampling sites is a function of the characteristics of the decay curve, i.e., the pollutant half-life, while the sensitivity analysis, cost, and a knowledge of parameter variability dictate the number of samples of a given type to be collected. The investigator needs to determine over what distance and time the compound of interest can be detected. This will be accomplished through a knowledge of the pollutant loading, flow

TABLE 1-5. DESIGN PROBLEMS AND POSSIBLE SOLUTIONS

| Problem | Possible Solutions |
|---|---|
| Multiple sources of loadings | Conduct study downstream of multiple sources--calculate loadings from cross-sectional transects<br>or<br>Measure all major sources but estimate minor sources<br>or<br>Avoid multiple loading sites. |
| Dilution of the water of interest | Account for differences between dilution effects and degradation/volatilization/sorption effects by using absolute dye concentrations, i.e., the reduction of the concentration of dye due to dilution water is proportional to the amount of dilution. Therefore, one can estimate the reduction of the compound of interest due to dilution alone.<br>or<br>Avoid, if possible. |
| Tracking long lived compounds in rivers | Tracking long-lived compounds through several half-lives in rivers is impractical due to dilution effects or multiple sources. Therefore, compounds with long half-lives may require lake or pond validation. |
| Movement of biota into and out of the zone of polluted water | Select territorial species (sunfish rather than trout). |
| Calculate water compartment volume when dimension data are not available | For flowing waters use dye travel time multiplied by the mean discharge rate to calculate the volume of a water compartment. For small pond or water bodies use dilution of a known amount of dye to calculate volume. |
| Defining lower boundary of sediment compartments | Use depth of detection of compound of interest<br>or<br>Use depth of detection of synthetic compound. |
| Gaging data not available | Install weirs<br>or<br>Use time to fill buckets<br>or<br>Use dye dilution techniques. |
| Nitrogen or phosphorus as limiting nutrients | Measure nitrogen and total phosphorus to detect abnormally low levels. |

rates, decay rates, and the detection limit for the compound of interest. See Appendix A for an example of how time and distance determinations were calculated for phenol in a river study.

The goal of any field validation study is to collect sufficient data to accurately describe the pollutant decay curve through several half-lives or the steady state concentration of a pollutant and the environmental conditions which influence the pollutant concentration over time. True steady state conditions are rarely achieved and, therefore, difficult to find. It may be possible to find certain holding ponds which closely approximate steady state conditions. However, a more practical solution may be to conduct small lake or pond studies by dosing the waterbody with a single input of a pollutant or pollutants and describing the decay curve or curves by repeated sampling over time. This type of study should be conducted in lakes or ponds which have complete mixing.

Even models with steady state assumptions can be manipulated to give downstream concentrations in pond tests by dummying in plug flow conditions (no mixing of the water of interest with the dummy water volumes used to create "flows"). Therefore, the model would predict various concentrations in downstream compartments as a function of distance. Since distance and time can be equated under "plug flow" conditions, e.g., one kilometer downstream equals one hour of travel time, this method can be used for steady state models to construct pollutant decay curves. In addition, computer codes of steady-state loading models can be modified to accept non-steady loadings. For example, a new version of EXAMS (EXAMS II or "Spike EXAMS") is currently available. EXAMS II allows one to predict environmental pollutant concentrations over time from single or multiple loading(s) of a specified pollutant mass at specified time(s).

Pollutant decay curves are commonly described by exponential rather than linear curves with the following general form:

$$C_F = C_o E^{-Kt}$$

where: $C_F$ = Final concentration

$C_o$ = Initial concentration

$K$ = Combined loss rate

$t$ = Time elapsed between the initial and final concentrations.

To accurately describe any decay curve with a given number of points it is optimal to have known points which represent equal changes in pollutant concentration and encompass the entire curve (Figure 1-4). Therefore, if an exponential curve is expected in a validation study, and if the physical properties of a specific site do not dictate compartment size, it is advantageous to have more sampling points in the initial phase than the tail portion of a curve. Obviously, little information would be provided by a number of sampling points in the tail portion of the curve where concentration does not vary to an appreciable extent over time or space. A geometric spacing of compartments may be convenient to use. Additional sampling

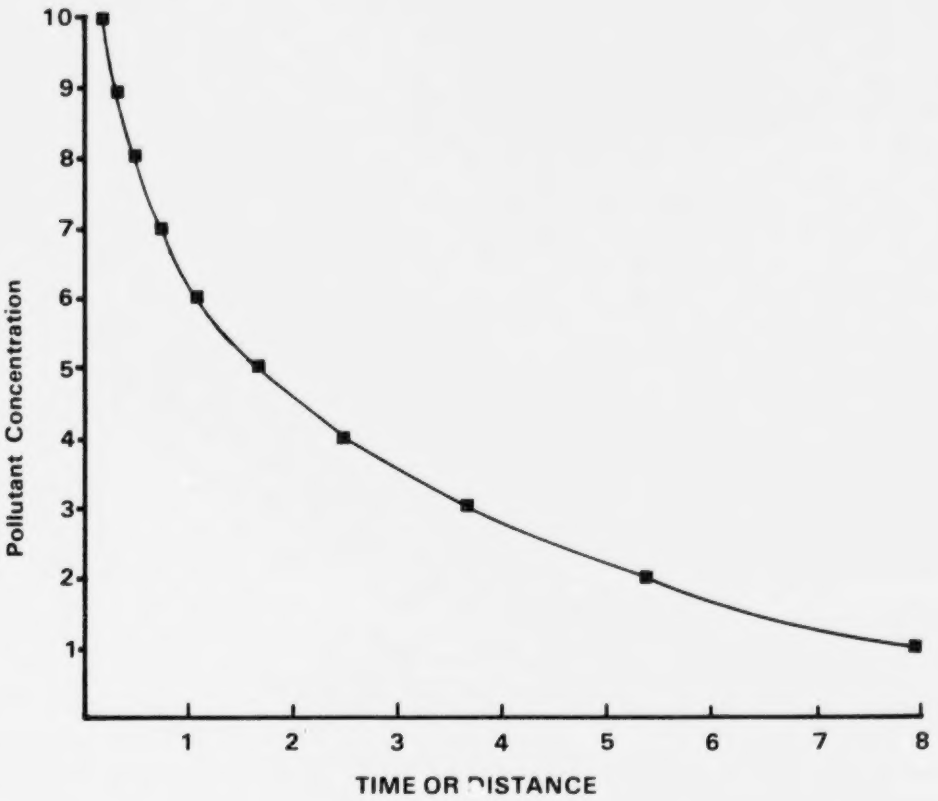


Figure 1-4. Pollutant decay curve.

points may be included after the initial sampling points are selected, in order to verify that there are no anomalies in the decay curve.

Fate and transport models may assume that a compartment is a completely mixed box (homogeneous) where a single parameter value represents conditions throughout the entire compartment. An investigator may simulate compliance by using average values which are representative of true compartment mean values. Calculation of simple mean values for parameters which vary over a large range in a short period may cause substantial input data bias which would invalidate the test of the model. For example, pH in a pond system may vary between 7 and 9 over a diurnal period. Compounds undergoing fast base but insignificant neutral hydrolysis would be degraded at pH 9 but not degraded at pH 7. It would be necessary to weight the pH value by the hydrolysis rate to reflect the shifting hydrolysis rates in an average pH value. This could be done by averaging the pseudo-first-order rate constants generated from model simulations based on continual sampling of pH values over a diurnal period, and adjusting the pH input value such that the model output would equal this average rate constant. Also, an investigator can reduce compartment size to reduce compartment variability so that an estimate of the true compartment mean is easier to obtain.

Although there are many possible designs to estimate pollutant means within a given water compartment for river or pond studies the following are offered to aid an investigator:

## Well-Mixed Rivers

1. Collect single grab sample at the middle of the compartment. This method assumes that the compartment is homogeneous or that the pollutant gradient is approximately linear from the upstream to the downstream boundaries of the compartment.

2. Collect depth and flow integrated samples at equally spaced points along a stream transect at the middle of a compartment. All samples would then be composited. The number of points (depth flow and flow integrated samples) is a function of stream width. This method assumes vertical, horizontal, or flow gradients exist at the mid-compartment transect. Depth and flow integrated samplers can be obtained from the Federal Inter-Agency Sedimentation Project, St. Anthony Falls Hydraulic Laboratory, 3rd Avenue and Hennepin Island, Minneapolis, Minnesota, 55414.

3. Collect vertical, horizontal and flow composite samples, as above, along transects at the upstream and downstream boundaries of a compartment. The data obtained from the transects can be averaged to obtain a mean parameter value. This method assumes a nonlinear pollutant gradient through the compartment.

## Poorly Mixed River

1. Collect discrete vertically integrated samples at points along a transect. Also, at the verticals collect mean discharge and total depth data. The stream is then divided into sections (two verticals represent the boundaries of a section) (Figure 1-5). No more than 10 percent of the total flow should pass through a given section. By this method one can calculate the pollutant concentration weighted by volume (PC) at a transect as follows:

$$PC = \frac{\sum_{i=1}^{n} V_i C_i}{\sum_{i=1}^{n} V_i}$$

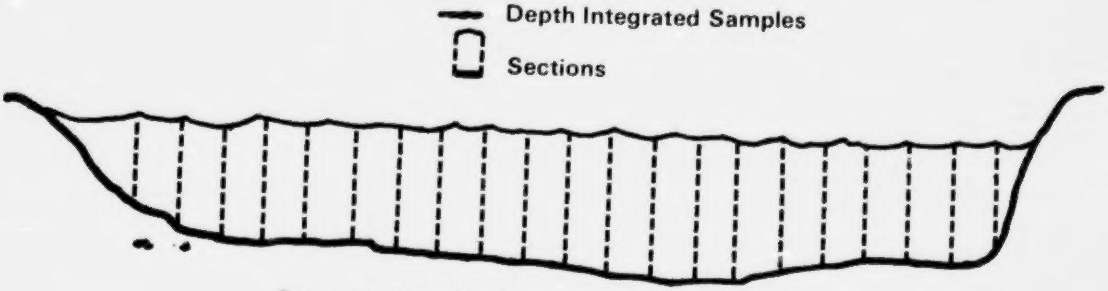
Where n = the number of sections

$V_i$ = the volume of section i

$C_i$ = pollutant concentration of section i (average of two verticals)

The pollutant concentration calculated can then be compared to the model's predicted value. Such transects could be located at the middle of a compartment or at the upstream and downstream boundaries of a compartment as described for well mixed rivers. Methods to measure stream discharge are presented in the Physical Transport section of this report.

2. Collect depth and flow integrated samples at the verticals described above. All depth and flow integrated samples would be composited to determine a pollutant concentration at the transect. Discharge data may still be collected to assure that the verticals are properly spaced and/or to satisfy physical transport input requirements.



Cross section of a river showing sections defined by depth integrated samples

Figure 1-5. Cross section of a river showing sections defined by depth integrated samples.

Ponds

1. Collect a single depth integrated sample. This assumes nearly complete mixing but allows for some minor thermal stratification.
2. Collect depth integrated samples at points along two transects at right angles to each other to account for horizontal gradients. The depth integrated samples may be averaged as composited.
3. Collect depth integrated samples at points on a grid system. The depth integrated samples can be averaged as composited.

Input parameter values may also be collected at the locations described above. However, additional sampling points may be required dependent upon the given parameter to represent its true compartment mean value.

Quality Assurance

The purpose of sampling in field validation of models is to provide quantitative environmental input data to the model and to collect field residue data that can be compared to the levels predicted by the model. Such field programs usually include the following operational steps:

Planning
Sample Collection
Sample Preservation
Sample Transport
Sample Storage
Sample Preparation
Sample Analysis
Data Acquisition
Data Manipulation
Data Interpretation
Reporting

To obtain valid data, an overall quality assurance (QA) program must apply quality assurance to all pertinent operational steps. In addition to the usual analytical and equipment QA procedures, a comprehensive QA program should include details on the reliability of the sampling program. Sampling schemes, data analysis strategies, and the objectives of the sampling program must be well defined for a statistician to assist in the development of an efficient collection program.

The importance of quality assurance is such that it is the EPA's policy that all intramural and extramural EPA funded projects involving environmental measurements must have an approved QA plan. Field validation of any aquatic fate and transport model for EPA by contract, grant or inhouse effort must conform to this requirement. The required format for project plans is given in "Interim Guidelines and Specifications for Preparing Quality Assurance Project Plans" from the Office of Monitoring Systems and Quality Assurance (U.S. EPA 1980a). Special items that supplement the guidelines are addressed below.

## Quality Assurance References

EPA's "Handbook for Analytical Quality Control in Water and Wastewater Laboratories", (U.S. EPA 1979a) addresses in detail the following areas: laboratory facilities, instruments, glassware requirements, and reagents. It further deals with control of analytical performance, data handling and reporting. Separate chapters are devoted to the special requirements for trace organic analysis, water and wastewater sampling, microbiology, aquatic biology and safety.

The "Quality Assurance Guidelines for Biological Testing" (U.S. EPA 1978) discusses the following elements of quality assurance: QA policy and objectives, design and analysis of experiments, sampling, precision and accuracy of tests, physical environment of research, chemicals and reagents, control of performance, and data handling and reports.

The "Handbook for Sampling and Preservation of Water and Wastewater" (U.S. EPA 1982) was developed for guidance on field monitoring required under the National Primary Drinking Water Regulation, the National Pollutant Discharge Elimination System, section 304(h) of the Clean Water Act, and the consent decree for priority pollutants. The handbook addresses the sampling of waters and wastewaters, such as industrial/ municipal wastewaters, agricultural run off, surface waters, and sediments, as well as flow monitoring, handling and preservation methods.

Detailed analytical procedures have recently been proposed by the U.S. EPA (1979b) for determining the concentration of 113 organic toxic pollutants in water. Methods 601-613 apply to the analysis of individual compounds or groups of chemically similar compounds. Methods 624 and 625 are GC/MS procedures for the analyses of the same compounds. The proposed methods cover calibration of instruments, quality control, sample collection, preservation and handling, sample extraction and analyses, and calculations. Revisions of the above methods appear in "Test Methods, Methods for Organic Chemical Analysis of Municipal and Industrial Wastewater" (Longbottom and Lichtenberg 1982). The majority of the revisions were made for clarification or to add additional flexibility for the analyst. Finalized procedures are to be published in the Federal Register in 1984.

Another source of EPA QA procedures is the "Manual of Analytical Quality Control for Pesticides and Related Compounds in Human and Environmental Samples" (Sherma 1981). A general description of pesticide residue analytical procedures is provided following a discussion on inter- and intra-laboratory quality control. Also covered are gas chromatograph procedures and troubleshooting, and procedures for analysis of samples including extraction, isolation and confirmation of pesticide residues. Although the manual deals primarily with pesticides, many of the procedures and recommendations apply to the analysis of any organic chemical.

There are many other sources of quality assurance procedures. Other EPA QA procedures are referenced in "The Quality Assurance Bibliography" (U.S. EPA 1980b). Many of these publications are available from the EPA, while the others are available from the National Technical Information Services in Springfield, Virginia.

## Evaluation of Literature and Unpublished Data

Part of the data used in validation may have been recorded in the past by different researchers in a variety of studies. While no rigid apriori criteria for acceptance or rejection of these data can be imposed, it should be stressed that they must be closely scrutinized. In many instances, data may be of limited value or even useless because precision and accuracy were not reported, or because of inadequate reporting of other parameters.

## Supplemental Data Acquisition

Whenever samples are collected at field sites, a variety of parameters important for interpretation and correlation of all data must be recorded. These parameters may include: sampling site location (coordinates, site number), sampling depth, flow data, date and time of day, meteorological conditions (air temperature, wind speed and direction, percent cloud cover, precipitation, fog), water temperature, water quality parameters (to be determined in the lab or field from collected samples or with contact sensing techniques: pH, conductivity, turbidity, color, dissolved oxygen, etc.). These supplemental data may help the researcher to recognize and explain data trends.

## Sampling

Sampling should be highly coordinated to collect a maximum of required samples per sampling trip. It is impossible to give directions covering all conditions, and the choice of sampling technique must often be left to the analyst's judgment. However, samples should be truly representative of existing conditions. This can sometimes be achieved, depending on circumstances, by making composites of samples that have been collected over a period of time, or at different sampling points. Composite samples should be replicated so that an estimate of field variation is obtained for each sampling time.

All sample containers should be sealed and labeled before they are shipped to the laboratory. Pertinent information should be recorded on a sample tag, e.g., sample, number, date and time taken, source of sample, preservative, analyses to be performed, and name of sample collector.

EPA approved procedures should, wherever possible, be used in collecting, preserving and analyzing samples. Many field sampling procedures, approved and unapproved, will be discussed at length in the subsequent sections. The references frequently provide information on the precision and accuracy of sampling, sample preservation procedures, information on container selection, etc., and are valuable sources of information on QA procedures. A complete list of EPA approved and tentatively approved test procedures related to aquatic sampling and analysis was published in the Federal Register (U.S. EPA 1979b). Also included was a table on approved containers, preservation procedures and holding times.

## STEP 6f: Compare Model Performance With Acceptance Criteria

## Data To Be Compared

The data to be compared are two sets of estimates of the amount or concentration (called Y) of pollutant in a study area. One set of estimates is the results of the field sampling (called c); the other set of estimates is the output of the fate and transport model (called Y). The general output from this type of model is a two-dimensional array of pollutant estimates, i.e., a matrix $\{\hat{Y}_{ij}\}$. The first index i runs over the media such as water, particulate material, biota, dissolved materials, etc. The second index j runs over the compartments (spatial grid) that describe the river or lake. If the pollutant of interest uses several media in its transport and the river or lake requires several compartments for adequate description, then there are many model estimates, one for each medium within each compartment. The field sample estimates must have the same dimensionality for comparison. If the pollutant uses only one medium in its fate and transport over the compartments, or if the body of water is homogeneous enough to be represented by one compartment, the matrix of estimates becomes a one-dimensional vector. In summary, there are two estimates (model outputs and field sampling statistics) to be compared and the estimate may be zero (scalar), one (vector), or two (matrix) dimensional arrays.

## Graphical Comparison

For a one or two-dimensional array, plot both the model estimate and field statistics on one graph for comparison. Each medium would be plotted on a separate graph and plots inspected for similarity of shape. Patterns of similarity to be expected would include asymptotic behavior at the same extremes, similar points of inflection, or relative maxima or minima at similar times or distances. These curves may be die-away curves and could be made linear by taking the natural log of the concentration. Linearization would simplify comparison of the curves. Therefore, linearize, if necessary and least square fit the data to a regression line. Confidence around the regression line can be calculated as follows:

$$CL\ (\gamma) = \hat{c} \quad t\ S_{\hat{c} \cdot d} \sqrt{1 + \frac{1}{N} + \frac{(d-\bar{d})^2}{\sum (d-\bar{d})2}}$$

where $CL$ = confidence limits

$\gamma$ = population parameter of amount or concentration of pollutant

$\hat{c}$ = regression line estimate of amount or concentration of pollutant via field observations

$t$ = t statistic for appropriate $\alpha$ and degrees of freedom

$S_{\hat{c} \cdot d}$ = standard deviation of $\hat{c}$ for fixed d

$d$ = distance or time for die-away

The regression line is plotted as a solid line in Figure 1-6 and the confidence curves plotted as dashed lines. The horizontal axis of Figure 1-6 is time or distance and the vertical axis the natural log of concentration or amount of pollutant. Time would be the dimension of die-away for a one time insult of pollutant to a pond while distance down stream would be the dimension of die-away for a continuous insult to a river.

A confidence interval about the regressed line of model estimates ($\hat{\gamma}ij$) comparable to the confidence interval about the regressed line of observed estimates ($cij$) is needed for comparison. However, replicate outputs from a deterministic model run with the same input values would produce one constant value and the standard deviation of the replicated output for a fixed set of inputs ($S\hat{\gamma} \cdot \vec{x}$) would be identically zero and would generate a confidence band of zero area. O'Neill and Gardner (1979) suggest that the sample variation of the inputs be used to generate a multivalued replicate output. That is, holding our distance or time input (d) constant at the point d, the model inputs ($\underset{\rightarrow}{X}$) have a range defined by their sampling errors ($\underset{\rightarrow}{S}$). Then, by rerunning the model for many combinations of the inputs randomly varied (Monte Carlo technique, Hoffman and Gardner in press), over their ranges would generate a multivalued sample of model outputs. The regression fitting of these samples of model outputs gives a regression line and a standard deviation $S\hat{Y}\cdot d$ for confidence curves about that regression line. Calculating $S\hat{Y}\cdot d$ by this technique may be a measure of only the dispersion of the intermediate inputs and may be an underestimate of the dispersion of the process being modeled; however, for a deterministic model it is the best available method. The Monte Carlo technique is "easier said than done;" however, some modelers have suggested building it into their models. With a $S\hat{Y}\cdot d$ for the regression on model estimates, confidence curves can be computed as was done for the regression line for the field observations. The regression line of model estimates is plotted in Figure 1-6 as a broken line (--) with dotted line confidence curves.

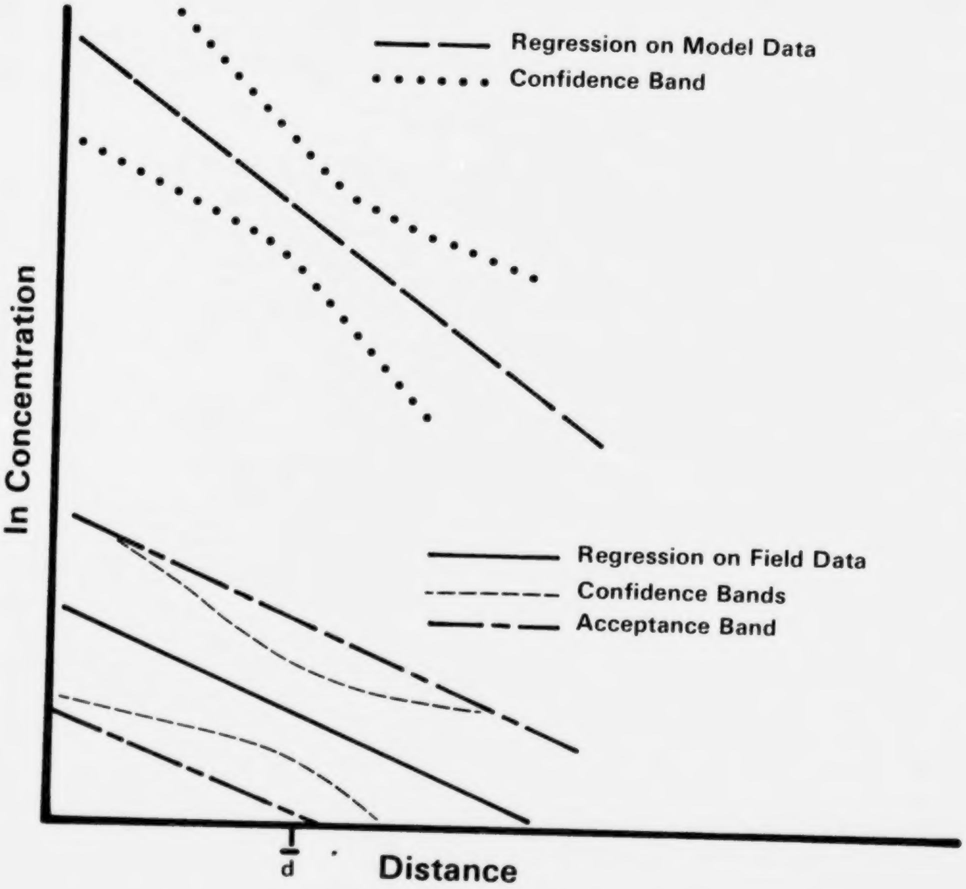


Figure 1-6. Regression lines and confidence bands for model and field data with acceptance band.

Lastly, the acceptance criteria discussed in the selection entitled Development of Acceptance Criteria for Verification, describes an "acceptance interval" about the true pollution values $Y$. Since the true $Y$ are unknown, the acceptance interval will be about the field sample estimates $c$. (It should be about the confidence interval of the field sample.) If the acceptance criteria were $1/2Y$ to $2Y$, then the acceptance interval for a linearized model of $c$'s would be plotted as the — - — line in Figure 1-6.

Figure 1-6 will show whether the modeled and observed lines are unusably different, or basically the same line with minor differences in intercept and slope, or within acceptance criteria. In Figure 1-6 the modeled output lies outside both confidence limits and acceptance criteria. One would conclude from this that the model was invalid and unacceptable for this pollutant and site. If the modeled and observed lines lie within each other's confidence curves, statistical comparisons should be done.

Other less direct but more diagnostic tests are the plotting of residuals ($E_{ij} = \hat{Y}_{ij} - c_{ij}$) or differences against time or distance ($d$), modeled concentration ($\hat{Y}_{ij}$), and observed concentration ($c_{ij}$). The difference of the modeled output minus the field observations plotted against distance or compartments would show cumulative error or bias. The horizontal axis is distance or time and the vertical axis would be differences or errors (Figure 1-7). There would be a graph for each media. The differences of a good fit should be random with a mean of zero. If the differences appear random but their average is non-zero, there is a bias in the model or the field data. If there is an increasing magnitude to the differences, there is a cumulative error in the model, or a negative cumulative error in the field observations.

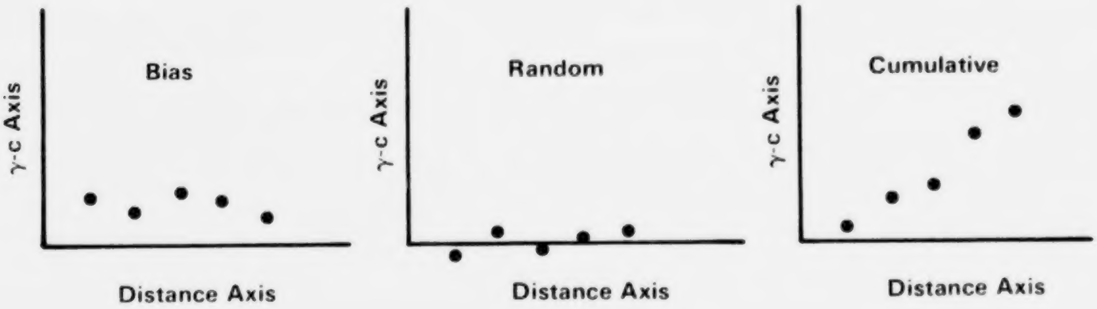


Figure 1-7. Graphic error analysis.

Next the differences should be plotted against media. Now the horizontal axis is media and there would be a plot for each compartment. This would show bias or cumulative error over media. Again, the differences or errors could be plotted against the observed estimate $c$ or the model estimate $\hat{Y}$ to see if the errors were observed concentration dependent or model concentration dependent. Random error is acceptable if unbiased and small variance, but cumulative error is more restrictive. A model with a cumulative error might be usable for a site with few compartments or a pollutant with rapid die-away. A model may be usable for one site and chemical but not usable for other sites or pollutants.

Finally, a simple but statistically definitive plot can be prepared which compares observed points to predicted model output. This is accomplished by computing confidence intervals (Sokal and Rohlf 1969) about the observed points on a die-away curve, and plotting those points, including the confidence about the points, on the same plot. The degree of observed and predicted (model generated) overlap can be evaluated based upon the graphical overlap of calculated confidence intervals with the predicted die-away. To perform this type of analysis it is necessary to replicate field sampling for the pollutant for each point that is to be compared to the predicted die-away.

### Statistical Comparisons

The t-test (Steel and Torrie 1960) for equality of means with unequal variance for the point comparisons and Hotelling's T2-test (Morrison 1967) for the vector comparisons would be statistically appropriate, but the needed variances are not available because no ecological models output the variance with their estimates. The variance of the model theoretically could be estimated by the Monte Carlo method discussed in the Graphical Comparison paragraphs, but in practice there would be problems of convergence and sample size. The variance of the field study's sample statistics may be estimatable from the observations.

Correlation coefficients can be calculated which will test for a linear relationship between observed and model generated values. This test will indicate if the points are related by a scale factor and an offset rather than absolute equality. The correlation coefficient must always be tested for significant differences from zero. For small sample sizes, apparently large correlations are not different from zero (i.e., an r of 0.8 is not different from zero for an n of 5, Table A13 Steel and Torrie 1960). This test can only be done if the modeled points and field samples points have the same abscissa (time or distance value). Strong correlations indicate that differences amoung observations can be explained by the model, while weak correlations indicate that differences among observations are controlled by factors unaccounted for by the model (Hoffman and Gardner 1983).

For a field study, the amount of a pollutant in a medium within a compartment is a continuous variable (U.S. EPA 1978). From the modeling point of view, the amount of pollutant might be thought of as the number of units of pollutant being distributed to various boxes (media within compartments, or media within a compartment, or medium across compartments). Then the count of pollution units per box would be distributed as a multinomial model, and the comparison of two estimates ($\hat{Y}ij$, cij) of pollution units frequencies can be done by the standard test for equality of multinomial frequencies (the chi-square test). The chi-square test is easily used, generally known and does not require estimates of variances (Steel and Torrie 1960). The chi-square loses power if there are fewer than four comparisons of observed (cij) and modeled ($\hat{Y}ij$) values (Cochran 1954). The experimental design planning must provide adequate number of modeled and observed estimates for comparison ($\geq 4$). Pollutants with few pathways in a homogeneous site may require more sampling locations (more j) for concentration (cij, $\hat{Y}ij$) comparison than for precision of model inputs. The chi-square test cannot have expected values ($\hat{Y}ij$) less than one count (Cochran 1954). The combinations of media(i) and compartments(j) that have zero expectation ($\hat{Y}ij = 0$) must be pooled or omitted. Zero for the pollutant count would be the background level or the detection limit whichever is larger. The degrees of freedom will be the number of boxes with non-zero $\hat{Y}ij$ minus one.

The null hypothesis states that the two sets of counts of pollutant amounts are the same and the apparent differences are not greater than could be expected from chance. The acceptance of the null hypothesis sustains but does not prove the validity of the model. The alternative hypothesis states that the two sets of counts of pollutant amounts are different and the differences are greater than could be expected from chance. The acceptance of the alternative hypothesis would invalidate the model for this use. The test statistic is mathematically stated as follows.

Let $\Phi$ = test statistic

$\hat{Y}_{ij}$ = model estimate of counts of pollutant in medium i of compartment j

$c_{ij}$ = field test sample statistic of counts of pollutant in medium i of compartment j

$\alpha\chi^2 df$ = chi-square table value for 1- probability with df degrees of freedom.

$$\Phi = \sum_{\text{compartments}} \sum_{\text{media}} \frac{(c - \hat{Y})^2}{\hat{Y}}$$

Note the double summation is for a two dimensional array or matrix and if there were i media within j compartments the summations would be

$$\Phi = \sum_{j=1}^{j} \sum_{i=1}^{i} \frac{(c - \hat{Y})^2}{\hat{Y}}$$

The double summation can be for a one dimensional array or vectors for i media within a compartment the summations would be

$$\Phi = \sum_{j=1}^{1} \sum_{i=1}^{i} \frac{(c - \hat{Y})^2}{\hat{Y}}$$

or for medium across j compartments the summations would be

$$\Phi = \sum_{j=1}^{j} \sum_{i=1}^{l} \frac{(c - \hat{Y}).^2}{\hat{Y}}$$

$$\Phi \leq \alpha X^2 df \rightarrow \text{no reason to reject } H_o$$
$$\Phi \overline{>} \alpha X^2 df \rightarrow \text{accept } H_1$$

If the test statistic is less than or equal to the chi-square critical value for a chosen probability and the appropriate degrees of freedom, the null hypothesis is sustained and the model has passed the field test. However, each field test is only a part of the complete validation process. If the test statistic is more than the chi-square critical value, the alternative hypothesis must be accepted and the model has failed this field test.

Regression Analysis--

If the model and observed lines laid within each others' confidence curves as suggested for the first test of the Graphic Comparison section, an appropriate statistical comparison is discussed on pages 173, 174 of Steel and Torrie (1960). The test requires residual and regression sum of squares. These are printed out by any regression program but three regressions must be run: (1) model estimates regressed on time or space unit, (2) field estimates c regressed on time or space unit, (3) pool of model and field estimates regressed on time or space unit. The null hypothesis states there is no significant difference between the regression equations, and the alternative hypothesis states that the two regression equations are different. The retention of the null hypothesis sustains but does not prove the validity of the model. The acceptance of the alternative hypothesis would invalidate the model for this use. The test statistic is mathematically stated as follows:

Let TS = test statistic

where SS-REG($\hat{Y}$) = sum of squares regression for the regression of model estimates on time or distance.

SS-RES($\hat{Y}$) = sum of squares residuals for the regression of model estimates on time or distance.

SS-REG(c) = sum of squares regression for the regression of observed estimates on time or distance.

SS-RES(c) = sum of squares residuals for the regression of observed estimates on time or distance.

SS-REG(Pooled) = sum of squares regression for the regression of modeled and observed estimates pooled together.

SS-RES(Pooled) = sum of squares residuals for the regression of modeled and observed estimates pooled together.

$$TS = \frac{\text{SS-REG}(\hat{\Upsilon}) + \text{SS-REG}(c) - \text{SS-REG}(\text{Pooled})}{[\text{SS-RES}(\hat{\Upsilon}) + \text{SS-RES}(c)]/(n\hat{\Upsilon} + n_c - 4)}$$

$TS \leq \alpha^{F} 1, n \;\; + n_c - 4 \rightarrow$ no reason to reject $H_o$
$TS \overline{>} \alpha^{F} 1, n \;\; + n_c - 4 \rightarrow$ reject $H_o$, accept $H_1$

If the test statistic (TS) is less than or equal to the F-critical value for a chosen probability ($\alpha$) and the appropriate degrees of freedom ($n\hat{\Upsilon}$ + nc-4), the null hypothesis is sustained and the model has passed the field test. If the test statistic is greater than the F-critical value, the alternative hypothesis must be accepted and the model has failed this field test.

Another regression analysis, first used by economic modelers (Cohen and Cyert 1961), is useful for evaluating agreement of model output and observed data. This test is appropriate for deterministic modeling but not for stochastic modeling (Aigner 1972). The null hypothesis states that the regression line of model estimates ($\hat{\Upsilon}$) on field data (c) has zero intercept and slope of one. The retention of the null hypothesis confirms the validity of the model. The alternative hypothesis states that either the intercept is not zero or the slope of the zero-intercept model is not one. This would imply that the model failed the field test.

To test the intercept and slope of a regression line, the number of observations should be at least twenty or thirty and the coefficient of determination ($R^2$) should be high ($\geq .80$). The tests are not independent and require two regression models ($\overline{\Gamma} = bC$ and $y = a + bc$). First, the intercept (a) of the model $\Upsilon = a + bc$ should be tested for equality to zero ($a = 0$).

If the test is omitted on your stat-package, run both a zero-intercept and intercept regression and compute this test statistic:

Let $TS$ = test statistic
$\Gamma$ = model output
$\overline{\Gamma}$ = average of model output
$\Upsilon = \Gamma - \overline{\Gamma}$
$C$ = field observations
$\overline{C}$ = average field observations
$c = C - \overline{C}$

$$TS = \frac{n^{\;2} + \text{SS-REG}(\Upsilon, c) - \text{SS-REG}(\Gamma, C)}{\text{SS-RES}(\Upsilon, c) \,/\, (n-2)}$$

where n = number of pairs of observations

SS-REG(Υ,c) = the sum of squares regression on the intercept model

SS-REG(Υ,C) = the sum of squares regression on the zero-intercept model

SS-RES(Υ,c) = the sum of squares residual on the intercept model

$$TS \leq {}_{\alpha}F_{1,n-2} \rightarrow \text{a not different from zero}$$

$$TS > {}_{\alpha}F_{1,n-2} \rightarrow a \neq 0$$

If the calculated test statistic is less than or equal to the critical F-value, the zero-intercept model is correct and the slope of the zero-intercept model should be tested for equality to one. The test statistic would be calculated as follows:

Let TS = test statistic

b = slope of zero-intercept regression line ( $\Gamma = bC$)

$$TS = (b - 1.0) \quad \frac{(n-1) \sum C2}{\text{SS-RES } (\Gamma, C)}$$

The critical value is a two-tail t-test for $\alpha/2$ and n-1 degrees of freedom.

$$|TS| \leq {}_{\alpha}t_{n-1} \rightarrow \text{slope is not different from one}$$

$$|TS| > {}_{\alpha}t_{n-1} \rightarrow \text{slope differs from one}$$

If the absolute value of the test statistic is less than or equal to the critical value of t for $\alpha/2$ (two-tail) and n-1 degrees of freedom the null hypothesis is sustained and the field test confirms the model validity. If the intercept was different from zero the slope may still be tested for equality to one for diagnostic reasons but SS-RES (Υ,c) and (n-2) should be used in an analogous test of the intercept model. If the intercept was statistically different from zero or if the slope of the zero intercept regression line was statistically different from one, the model estimates disagree with the field observations.

In summary, the more obvious statistical tests (t and Hotelling T2) require more information (s, {S}) than available, but with appropriate qualifications the chi-square test or regression analysis are reasonably appropriate. Either can accommodate the variable dimensionality of the data. The regression approach will require a computer program with a zero-intercept option to manipulate the data, while the chi-square can be done on a hand-held calculator. The user should choose the method best suited to his resources.

## SUMMARY

Field validations of aquatic fate and transport models require the collection and quantification of numerous chemical, physical, and biological parameters over time for model input variables and model output variables. Because of the complexities associated with field validation a staggered approach (steps 1-6) has been suggested in this report (Table 1-1). However, one does not have to sequentially complete one step before proceeding to the next since many steps can be completed simultaneously. In addition, preliminary planning should include provisions to repeat experiments when performing validations in complex environments or with compounds that are subject to multiple fates.

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## MODEL INPUTS AND OUTPUTS

This part of the report deals with collection of the site specific input data required to run and evaluate models. Two types of model input data are required that are needed to describe the fate and transport processes and pollutant loading data. In addition, actual pollutant concentrations that correspond to those predicted by the model are required.

Table 2-1 summarizes specific model inputs for the EXAMS (Burns et al. 1982) and TOXICS (Schnoor and McAvoy 1981) model. Some of the PEST (Park 1980) model inputs are included under bioconcentration. The table also lists environmental inputs that are currently being developed for incorporation into models, and speculative parameters; those inputs known to be important to a process but for which the relationships have not been defined. The input loadings to aquatic fate and transport models are summarized in Table 2-2. The predicted model outputs for the EXAMS, TOXICS, and PEST models are provided in Table 2-3.

## TABLE 2-1. ENVIRONMENTAL INPUTS BY PROCESS, TO AQUATIC FATE AND TRANSPORT MODELS

| Environmental Input and Units | Currently* Used In | In Development | Future? |
|---|---|---|---|
| Biotransformation | | | |
| Temperature (°C) | E | | |
| Total Bacteria Pop. (Cells/ml) or (Cells/100 g dry sed.) | ET | | |
| Active Degrading Pop. (% of Total) | E | X | |
| Nutrients C/N, P (mg/l) | | | X |
| Acclimation State | | | X |
| PH (pH Units) | | | X |
| Dissolved Oxygen (mg/l) | | | X |
| Hydrolysis | | | |
| POH (pH Units) | E | | |
| PH (pH Units) | ET | | |
| Temperature (°C) | E | | |
| General Acids/Bases | | X | |
| Oxidation | | | |
| Temperature (°C) | E | | |
| Oxidant Concentration (moles/l) | E | | |
| Reaeration (cm/hr) | | | X |
| Suspended Particulate (mg/l) | | | X |
| Dissolved Oxygen (mg/l) | | | X |
| Dissolved Organic Carbon (mg/l) | | | X |
| Photolysis | | | |
| Depth (m) | ET | | |
| Chlorophyll (mg/l) | E | | |
| Latitude (degrees) | E | | |
| Cloudiness (tenths) | E | | |
| Dissolved Organic Carbon (mg/l) | E | | |
| Suspended Sediment (mg/l) | E | | |
| Spectral light intensity at surface | E | | |
| Altitude (m) | | X | |
| Temperature (°C) | | | X |
| Time of Day (24 hr. time) | | | X |
| Time of Year | | | X |

*See end of table, page 2-4 for footnotes.

(continued)

TABLE 2-1. (Continued)

| Environmental Input and Units | Currently* Used In | In Development | Future? |
|---|---|---|---|
| Ionization | | | |
| POH (pH Units) | E | | |
| PH (pH Units) | E | | |
| Temperature (°C) | E | | |
| Total Dissolved Solids (mg/l) | | | X |
| Ionic Strength | | | X |
| Volatilization | | | |
| Temperature (°C) | E | | |
| Compartment Dimensions, area and volume | E | | |
| Reaeration Rate (cm/hr) | E | | |
| Wind (m/s) | E | | |
| Slope (m/m) | | X | |
| Water Velocity (m/s) | | X | |
| Fetch | | | X |
| Sediment Sorption | | | |
| Organic Carbon Content (% of dry sediment) | E | | |
| Percent Water of Benthic Sediment $\frac{(100\ \text{Fresh Wt.})}{(\ \text{Dry Wt.}\ )}$ | ET | | |
| Bulk Density Benthic Sed. (g/cc) | ET | | |
| Suspended Sediment (mg/l) | ET | | |
| Compartment Dimensions & Areas | ET | | |
| Cation Exch. Cap. (meg/100 g dry sediment) | | X | |
| Anion Exch. Cap. (meg/100 g dry sediment) | | X | |
| Particle Size (mm) | | X | |
| PH of Sediment (pH Units) | | | X |
| Bioconcentration | | | |
| Total Biomass (mg/l or g/m$^2$) | ET | | |
| Planktonic Biomass (fraction of total) | ET | | |
| Fish (g/m$^3$) | PT | | |
| Water Bugs (g/m$^3$) | P | | |

*See end of table, page 2-4 for footnote.

(continued)

TABLE 2-1. (Continued)

| Environmental Input and Units | Currently Used In | In Development | Future? |
|---|---|---|---|
| Zooplankton (g/$m^3$) | P | | |
| Phytoplankton (g/$m^3$) | P | | |
| Particulate Organic Matter (g/$m^3$) | P | | |
| Floating Particulates Organic Matter (g/$m^3$) | P | | |
| Floating Macrophytes (g/$m^3$) | P | | |
| Dissolved Organic Matter (g/$m^3$) | P | | |
| Zoobenthos (g/$m^3$) | P | | |
| Chlorophyll a (mg/l) | | | X |
| Fish by Species (g/$m^3$) | | | X |
| Fish by Age or Size Class (g/$m^3$) | | | X |
| Periphyton (g/$m^3$) | | | X |
| Zoobenthos by Functional Group (g/$m^3$) | | | X |
| Temperature (°C) | | | X |
| Dissolved Oxygen (mg/l) | | | X |
| Macrophytes, Rooted (g/$m^3$) | | | X |
| Physical Transport | | | |
| Evaporation-(mm/month) | ET | | |
| Interflow ($m^3$/hr) | ET | | |
| NPS Sediment Load (kg/hr) | ET | | |
| NPS Water Load ($m^3$/hr) | ET | | |
| Percent Water of Bottom Sed. (100 x fresh/dry WT. sed.) | ET | | |
| Rainfall (mm/month) | E | | |
| Suspended Sediment (mg/l) | ET | | |
| Bulk Density Bottom Sed. (g/cc) | ET | | |
| Stream Inflow ($m^3$/hr) | ET | | |
| Stream Borne Sediment Inflow (kg/hr) | ET | | |
| Compartment Volume ($m^3$) | ET | | |
| Eddy Diffusivity ($m^2$/hr) | ET | | |
| Cross Section Area for Dispersive Exchange ($m^2$) | ET | | |
| Surface Area ($m^2$) | ET | | |
| Dist. Between Compt. Centers (m) | ET | | |
| Compartment Dimensions L, W, H (m) | ET | | |
| Sediment Bed Load (kg/hr) | ET | | |
| Planktonic Biomass (mg/l) | E | | |
| Water Velocity (m/s) | T | X | |
| Dissolved Organic Carbon (mg/l) | | | X |
| Bed Load by Part. Size Classes (%) | | X | |
| Total Organic Carbon (mg/l) | | X | |

E = EXAMS model suspended sediment settling velocity dispersive bed scour/resuspension

T = TOXICS model

P = PEST model (incomplete)

TABLE 2-2. POLLUTANT LOADING INPUTS TO AQUATIC FATE AND TRANSPORT MODELS

| Loading Input and Units | Currently Used In | In Development | Future? |
|---|---|---|---|
| Aerial Drift Loading (kg/hr) | E | | |
| Loading via Ground Water (kg/hr) | E | | |
| Rainfall Loading (kg/hr) | E | | |
| Loading via Stream Flow (kg/hr) | ET | | |
| Loading via NPS Flow (kg/hr) | E | X | |
| Loading via Particulate Organic Matter (kg/hr) | T | X | |
| Loading via Suspended Sed. (kg/hr) | | X | |
| Loading via NPS Sed. (kg/hr) | | X | |
| Loading via Bed Load (kg/hr) | | | X |
| Loading via Plankton (kg/hr) | | | X |
| Loading via Fish, Birds (kg/hr) | | | X |
| Loading via Point Sources (kg/hr) | E | | |

E = EXAMS model (steady state)
T = TOXICS model (time variable)

TABLE 2-3. POLLUTANT CONCENTRATIONS PREDICTED BY AQUATIC FATE AND TRANSPORT MODELS

| Model Output and Units | Currently Used In | In Development | Future? |
|---|---|---|---|
| Water, Dissolved (mg/l) | ET | | |
| Suspended Sediment (mg/kg) | ET | | |
| Biota in Water Column (mg/l) | E | T | |
| Sed. Pore Water (mg/l) | ET | | |
| Benthic Sediment-Sorbed (mg/kg) | ET | | |
| Benthic Biota ($g/m^2$) | E | T | |
| Water Column-Total (mg/l) | ET | | |
| Benthic Sediment-Total (mg/kg) | E | T | |
| Zooplankton ($g/m^3$ of $H_2O$) | P | | |
| Waterbugs ($g/m^3$ of $H_2O$) | P | | |
| Phytoplankton ($g/m^3$ of $H_2O$) | P | | |
| Macrophytes ($g/m^3$ of $H_2O$) | P | | |
| Particulate Organic Matter ($g/m^3$ of $H_2O$) | P | | |
| Floating Organic Matter ($g/m^3$ of $H_2O$) | P | | |
| Clay ($g/m^3$ of $H_2O$) | P | | |
| Fish ($g/m^3$ of $H_2O$) | P | T | |

E = EXAMS model
T = TOXICS model
P = PEST model

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# BIOTRANSFORMATION

## PROCESS DESCRIPTION

Microorganisms can adapt to a variety of environmental conditions and biotransform and/or biodegrade a very large number of organic chemicals. Biodegradation is defined as a biologically mediated reduction in complexity of a particular chemical by splitting off one or more constitutent groups or components. Whereas, biotransformation is an encompassing term which includes biodegradation and biologically mediated additions to the parent chemical. It has been stated that any compound which is synthesized biologically can be degraded microbiologically. However, many man-made compounds are strongly resistant to microbial degradation (recalcitrant) such as certain pesticides, hard detergents, petroleum hydrocarbons, and plastics (Alexander 1964).

Microbial transformation of a toxic substance may yield a product that is more or less toxic than the parent compound. In addition, transformation products in conjunction with the parent compound can show synergistic toxicities.

Although degradation might be accomplished by any living organism, microorganisms play the dominant role because of their high numbers and catabolic versatility, species diversity and metabolic rate per unit of weight. Algae, actinomycetes, protozoans, and fungi can all participate in the degradation of organics. Bacteria normally dominate, however, in the aquatic environment. Fungi often are important decomposers under acidic sediment conditions. Microbial decomposition of natural organics is normally accomplished for energy and to produce degradation products which can be used as cellular constituents. From 60 to 80 percent of the carbon in organic matter assimilated by bacteria is liberated as carbon dioxide and the remaining 20 to 40 percent is converted into cellular material. This material is the major source of bacterial biomass, most of which is devoured by protozoa and higher life forms in the aquatic environment (Tallon 1969).

Biological degradation of organic pollutants is often accomplished by a number of species sequentially in an "assembly line" decomposition. The first metabolic product then may serve as the substrate for another species and so on until complete mineralization has been accomplished. However, intermediate metabolic products are often produced which are resistant to further breakdown or are only slowly degraded in the aquatic environment.

Alexander (1964) lists the following factors which influence the biotransformation of organic materials:

1. Absence of essential growth factor - Growth would not occur in the absence of nitrogen or phosphorus.

2. Toxicity of the environment - This may result from the pollutant, biologically generated inhibitors (antibiotics) or toxins, high salt concentrations, extremes in pH, temperature, light, or pressure.

3. Structural characteristics of the molecule - Molecular configurations which do not permit the formation of an enzyme - substrate complex.

4. Inaccessibility of the substrate - The compound may exist in a micro-environment which prevents or lessens microbial attack, e.g., sorbed onto clay minerals or embedded within a matrix.

5. Inactivation of requisite enzymes - Enzymes may lose activity by sorption to clay minerals or may be inhibited by other substances (metals) in the environment.

6. Inability of the microorganism community to metabolize the compound because of some physiological inadequacy - An enzyme capable of degrading the compound may not exist or the substance may not be able to penetrate into the cells where appropriate enzymes do exist.

## ENVIRONMENTAL FACTORS

### Limiting Nutrients

Many microorganisms are adapted to sporadic occurrences of suitable energy sources (e.g., autumn leaf-fall, death of large animals, etc.) and can grow very rapidly when a suitable organic (energy-yielding) substrate is available. The limiting nutrient concept, derived from Liebig's law of the minimum, is that the nutrient that is least available relative to the growth of a given organism imposes primary limitation on the growth of that organism. Table 3-1 lists the nutrients required by certain microorganisms. The availability of carbon, nitrogen, and phosphorus frequently inhibit microbial growth.

### Dissolved Oxygen

The quantity of dissolved oxygen present in water influences the kinds of organisms and the rate of decomposition. Four groups of microorganisms may be distinguished according to their oxygen requirements (Rheinheimer 1974);

1. Obligate aerobes - which grow only in the presence of oxygen,

2. Microaerophiles - which grow optimally at low oxygen concentrations,

3. Facultative aerobes - which grow in presence or absence of oxygen, and

4. Obligate anaerobes - which grow only in the absence of oxygen.

The majority of aquatic bacteria are facultative aerobes. Molecular oxygen is vital for obligatory aerobes as it is necessary as a terminal hydrogen acceptor in respiration. Fluctuations of ambient oxygen concentrations normally do not affect obligatory aerobes. For example, the

TABLE 3-1. NUTRIENTS REQUIRED BY CERTAIN MICROORGANISMS

| | |
|---|---|
| 1. Energy Source | Organic compounds<br>Inorganic compounds<br>Sunlight |
| 2. Electron acceptor | $O_2$<br>Organic compounds<br>$NO_3-,NO_2-,N_2O,SO_4=,CO_2,Fe^{+++}$ |
| 3. Carbon source | $CO_2,HCO_3$ -<br>Organic compounds |
| 4. Growth factors | |
| a. Amino acids | Alanine, aspartic acid, glutamic acid, etc. |
| b. Vitamins | Thiamine, biotin, pyridoxine, riboflavin, nicotinic acid, pantothenic acid, -aminobenzoic acid, folic acid, thioctic acid, $B_{12}$, etc. |
| c. Others | Purine bases, pyrimidine bases, choline, inositol, peptides, etc.<br>N,P,K,Mg,S,Fe,Ca,Mn,Zn,Cu,Co,Mo,Cl,Si,B,Na,V,I |

Modified from Alexander (1961).

nitrate bacteria Nitrobacteria winogradski maintains its oxidation rate at dissolved oxygen levels from saturation down to 2 ppm. Only a further decrease of oxygen makes the oxidation rate drop. In contrast, obligatory anaerobes are impaired at very low oxygen levels (Rheinheimer 1974).

Anaerobic decomposition of organic matter is normally much slower than aerobic decomposition. There is a lower cell yield and degradation is incomplete under anaerobic conditions. Generally the end products of aerobic decomposition are carbon dioxide and water while anaerobic respiration often yields organic acids (Mitchell 1974).

## Concentration of Toxic Organic

The concentration of a toxic organic pollutant is an important factor influencing its degradation rate. At high concentrations an organic pollutant may demonstrate bactericidal or bacteriostatic properties whereas at low concentrations the organic pollutant may be readily degraded. Phenol is commonly used as a disinfectant at high concentrations (2 to 5 percent); however, it is readily used by bacteria as a substrate at low concentrations (Pelczar and Reid 1972). Any biological system can be overloaded with a toxic organic pollutant. For example, chlorodiphenyl oxide has a slower degradation rate at 9.2 mg/l than at lower concentrations (Branson 1978).

Besides, bactericidal and bacteriostatic affects, biotransformation rate constants may not be independent of chemical concentration (usually assumed in fate models). The biotransformation rate may change at low contaminant concentrations found in most natural environments. Unfortunately, most laboratory tests to determine biotransformation rates are conducted with concentrations of test chemicals far higher than those found in rivers, lakes and marine waters. Little attention is given to how the rate of transformation in artificial microcosms approximates the rate under natural conditions (Boethling and Alexander 1979).

## Temperature

Temperature is one of the most important environmental conditions determining degradation rates. The temperature coefficient of biological processes is sometimes expressed in terms of $Q_{10}$. This value is the ratio of the velocity constant of a process at a given temperature to the velocity constant at a temperature 10°C higher. Optimal temperatures for degradation and the response of degradation to different temperature can be reasonably predicted (Nesbitt and Watson 1980a).

Three groups of bacteria may be distinguished by their temperature tolerance. Most organisms are mesophiles (15° to 45°C) with an optimum range of 25° to 35°C. Psychrophiles grow best at temperatures below 20°C while thermophiles grow readily from 45° to 65°C (Alexander 1961). High concentrations of mesophiles and psychrophiles can be detected in many aquatic systems, while thermophiles are basically restricted to thermal springs. An increase in temperature results in an increased rate of biologically mediated decomposition, e.g., pesticide degradation (Lichtenstein 1972) and oil degradation (Westlake et al. 1978) by bacteria are increased at elevated temperatures.

## pH

The growth and reproduction of microorganisms are affected by the hydrogen ion concentration of the medium. Most bacteria can only grow within the pH range of 4 to 9 while the optimum for most aquatic bacteria is between pH 6.5 to 8.5. This corresponds to the pH range of most water bodies. There are more acidophilic fungi than bacteria; therefore, the proportion of fungi in the microflora increase in acid waters or sediments.

## Acclimation

There can be a considerable lag between the exposure of a new chemical to the organism and the initiation of degradation by microorganisms. This lag time exists because organisms must acclimatize to a new substrate in any of several ways. Cells may adapt by synthesizing new enzymes in response to new substrate added to the environment (enzyme induction). Second, a change in the environment may allow for the selection of mutant types. Third, a change in the environment may increase the population of existing organisms that grow on the added substrate (Brock 1966).

In nature, acclimation time may have a great influence on the rate of degradation since microorganisms may not have an opportunity to acclimate to a new chemical (Howard et al. 1978). This is particularly important in flowing waters that receive periodic discharges. Under these circumstances, attached organisms will only be exposed to a pollutant "slug" for a short time while planktonic forms traveling the "slug" will have a greater opportunity to acclimate. However, dilution effects may result in such low concentrations of the pollutant that the acclimation response may not be fully realized. Since exposure times to intermittent discharges are greater in lake or pond environments than in fast flowing streams, the probability for full acclimation is enhanced. However, continuous discharges provide the greater opportunity for microbial acclimation, regardless of the environment. Experiments to determine microbial degradation rates involving long time periods may allow development of a microbial population acclimated to the compound present. This can lead to apparent high rate constants. Perhaps even more significant, rate constants developed from short-term experiments may lead to apparent low rate constants (Branson 1978).

Many organic contaminants only occur at low concentrations (< 100 µg/l) in natural aquatic systems. Dickson et al. (1981) found no lag phase for napthalene and lindane biotransformation at concentrations ranging from 100 to 500 µg/l. However, experiments with phenol using the same concentration range demonstrated approximately a 3-day lag phase. Therefore, acclimation state may not be an important consideration at low contaminant concentrations for certain chemicals.

## Major Environmental Factors

Major factors governing microbial decomposition include temperature, pH, acclimation state, organic matter levels and sufficient levels of nitrogen and phosphorus. As a general rule, environmental modifications that favor microbial proliferation increase site specific degradation rates. Thus, a rise in temperature, increased available carbon and neutral pH, all tend to increase site specific degradation rates. Table 3-2 lists the major environmental factors that influence microbial degradation rates.

TABLE 3-2. MAJOR ENVIRONMENTAL FACTORS THAT INFLUENCE DEGRADATION RATES

Nutrients - Carbon, nitrogen, phosphorus
Temperature
pH
Dissolved oxygen concentration
Size and composition of the active microbial community
Acclimation state

## COMPOUND-RATE RELATIONSHIPS

Obviously, the specific organic chemical of concern governs the transformation rate under optimal environmental conditions for the given chemical. Half-lives vary from hours for certain compounds such as sugars, starches, etc., to months or years for other compounds such as certain chlorinated hydrocarbons or trisubstituted phenoxyaliphatic acids. In recent years considerable effort has been devoted to relating the chemical structure of a molecule to its microbial biodegradability. Although these investigations have been restricted to a limited number of compounds, a few generalizations can be made:

1. Short-chain aliphatic hydrocarbons are not as readily degraded as those of high molecular weight (Tallon 1969).
2. Straight-chain alkanes are degraded more rapidly than branched alkanes (Mitchell 1974).
3. Unsaturated aliphatics are more readily attacked than the corresponding saturated hydro-carbon (Tallon 1969).
4. The branched-chain alkyl benzene sulfonate (ABS) detergents are poorly degraded compared to linear alkyl sulfonates (LAS) detergents (Mitchell 1974).
5. A molecule is more resistant when a carbon atom in a chain is replaced by oxygen, sulfur, nitrogen, halogens, nitrile, or phosphorus (Tallon 1969).
6. Many aromatic hydrocarbons are strongly recalcitrant and frequently accumulate in the sediments; e.g., no organisms have been isolated that will grow with polycyclic hydrocarbons that contain more than three aromatic rings (Gibson 1978).
7. Comparable resistance to biotransformation of pesticides as a function of structure is presented below. The compounds are ranked from the most to the least resistant to microbial breakdown (Mitchell 1974).

    Chlorinated hydrocarbons
    Trisubstituted phenoxyaliphatic acids
    Disubstituted phenoxyaliphatic acids
    Monosubstituted phenoxyaliphatic acids
    Long-chain phenoxyaliphatic acids
    Organophosphates
    Aliphatic acids

## BIOTRANSFORMATION RATE CONSTANT

Biotransformation rate constants have been expressed as first order and as second order rate constants (pseudo-first order). First order rates need only chemical concentration to describe biodegradation although the importance of compounds, the character of the microbial population, and nonlinear responses over ranges of concentration are recognized (Boethling annd Alexander 1980, Larson 1980, Johnson 1980). Second order or pseudo-first order rate constants to describe biodegradation rates require bacterial population numbers and chemical concentration (Baughman et al. 1980). Apparently, heterotrophic microbial biomass is a major factor in biotransformation of chemicals in aquatic systems. However, others have found little or no relationship between degradation rates and estimates of biomass (Nesbitt and Watson 1980b, Dickson et al. 1981). Organic priority pollutants for which microbial degradation is a significant fate process are listed in Table 3-3.

## MICROBIAL METHODS

### Microbial Degradation Rate Constant

The microbial degradation rate constant is usually determined in the laboratory and, for the purposes of these guidelines, is considered a chemical input parameter. The rate constants which were developed under laboratory conditions which most closely approximate conditions at the validation site should be chosen. Factors to be considered in the selection are chemical species and concentration, microbial population and acclimation state.

For some toxic organics, such as phenol, this rate constant is extremely critical, i.e., the model outputs are very sensitive to a change in the rate constants. Three rate constants may be important depending upon the model, pollutant, biomass, etc. They are the degradation rates of the pollutant in the soluble, biosorbed, and sediment sorbed forms. The importance of the rate constants can be determined during the sensitivity analyses.

If rate constants are expressed as percent disappearance of a pollutant per unit of biomass (or cell count) per unit of time, both field and laboratory measurements for the rate constants of biomass or cell count must be identical or equivalent. The usual procedure has been to use standard plate counts (SPC) to estimate the number of cells per volume. Other means of measuring cell counts or biomass include direct count methods such as epifluorescence, the measurement of adenosine triphosphate (ATP), and the determination of bound lipopolysaccharide (LPS).

There are advantages and disadvantages to each of the above techniques of determining microbial populations. The most appropriate technique depends upon how well the measurement of biomass or cell count correlates with microbial degradation at the selected site. In the development of a biodegradation rate constant, biological lag time should also be determined.

### Acclimation State

An investigator should select the appropriate degradation rate constant which reflects the acclimation state of the bacteria at the selected site and

TABLE 3-3. ORGANIC PRIORITY POLLUTANTS WHOSE AQUATIC FATE IS SIGNIFICANTLY AFFECTED BY MICROBIAL DEGRADATION

**Pesticides**

Acrolein
Aldrin
DDD
Endosulfan and Endosulfan sulfate
Hexachlorocyclohexane
γ-Hexachlorocyclohexane (Lindane)
TCDD
2-Chloronaphthalene

**Monocyclic Aromatics**

Nitrobenzene
2,4-Dinitrotoluene
2,6-Dinitrotoluene
Phenol
2,4-Dichlorophenol

**Phthalate Esters**

Dimethyl phthalate
Diethyl phthalate
Di-n-butyl phthalate
Di-n-octyl phthalate
Bis (2-Ethylhexyl) phthalate
Butyl benzyl phthalate

**Polycyclic Aromatic Hydrocarbons**

Acenaphthalene
Acenaphthylene
Anthracene
Benzo [a] anthracene
Benzo [b] fluoranthene
Benzo [e] fluoranthene
Benzo [ghi] perylene
Benzo [a] pyrene
Chrysene
Dibenzo [a,h] anthracene
Fluoranthene
Fluorene
Indeno [1,2,3-cd] pyrene
Naphthalene
Phenanthrene
Pyrene

Source: Callahan et al. 1979.

the concentration of the chemical. Therefore, if a site only receives periodic discharges of the compound of interest, one would utilize a rate constant which was developed without regard for acclimation. Whereas, if the selected site receives continuous discharge, the rate constant should be developed with organisms which have been acclimated.

## Methods to Estimate Total Microbial Populations

### Water--

The standard plate count method can be used to estimate the viable aerobic and facultative anaerobic bacteria in an aquatic environment (Bordner and Winter 1978 and APHA 1980). An aliquot of the water sample or its dilution is pipetted into a sterile petri dish and a liquified, tempered agar medium added. The petri dish is then rotated to evenly distribute the bacteria. Theoretically, each bacterium present multiplies into a visible colony which is counted to estimate the bacterial population, However, the procedure does not yield the true number of bacteria since not all viable bacterial cells in the water sample can reproduce under a single set of culture conditions imposed in the test. Underestimates of bacterial density also occur because, 1) some microorganisms will not develop within the specified incubation period, 2) the procedure does not allow fastidious aerobes or obligate anaerobes to develop, and 3) clumps of organisms will appear as a single colony. Another disadvantage to the SPC method is the relatively short holding time. Sample analysis should be initiated as soon as possible to minimize changes in the bacterial population. If the sample cannot be analyzed at once, it should be refrigerated and analyzed within six hours (Bordner and Winter 1978). Incubation temperature and duration must be identical to those used to determine the laboratory based rate constants. This simple technique is a useful tool for determining bacterial density for fate and transport studies if, 1) the total bacterial population is capable of degrading the pollutant, or 2) the percent of the total population detected by the SPC is relatively constant between field sampling and rate determination tests.

Prescott et al. (1946) reported that the standard deviation of individual counts from plates with 30-300 colonies will vary from 0-30 percent. The plating error was 10 percent for plate counts within the 100-300 range. In addition to plating error, a dilution error of about 3 percent is expected for each dilution required. Large variations can be expected from high density samples, e.g., sewage. Laboratory personnel should be able to duplicate their plate count values on the same plate within 5 percent and the count of others within 10 percent.

Direct microscope counting methods can be used to estimate bacterial numbers in aquatic environments. The advantage of direct counts is that the total population is enumerated rather than some percentage of the total population as with the SPC method. Therefore, direct counts are generally much higher (1 to 3 orders of magnitude) than plate counts. The epifluorescence counting method is suggested (Watson et al. 1977). An epifluorescence microscope is employed to count bacteria that have been concentrated on membrane filters and stained with acridine orange. This method reduces errors of improper identification of detrital material versus bacterial cells commonly associated with previous direct count methods. Another advantage with this method is that water samples may be preserved for 2 weeks prior to examination. Also, the method seems to yield more precise information (less variance) than SPC methods. The method is relatively inexpensive (about 30 dollars per sample) and only requires about 1 hour to perform. Disadvantages include: specialized equipment is required (i.e., Zeiss standard microscope equipped with an epifluorescent illumination system containing a 100-W halogen lamp, a BG12 excitation filter, a LP510 barrier filter and an FT beam splitter), and the investigator cannot distinguish between viable and non-viable cells. This procedure would eliminate one of the difficulties associated with the SPC, i.e., detecting only a percentage of viable total population.

Biomass determinations eliminate the problems associated with SPC and direct counts but they possess other disadvantages. The biomass of microbial populations can be estimated by measuring the amount of cellular bound lipopolysaccharide (LPS), adenosine triphosphate (ATP), or limulus amebocyte lysatc (LAL).

Measuring ATP levels provides an estimate of the total viable planktonic biomass. ATP occurs in all living plant and animal cells and is not associated with non-living particulate material. The ratio of ATP to biomass varies from species to species and with the physiological state of a cell. However, the method can be used to estimate biomass (APHA 1980).

The ATP content of a water sample is determined by concentrating the organisms on a membrane filter. The ATP content of the organisms is extracted by boiling the filter in a buffer solution. The ATP thus extracted is reacted with luciferase in the presence of oxygen and magnesium to produce water, luciferin, adenosine monophosphate (AMP), inorganic polyphosphate (PPi), and light. The amount of light emmitted is proportional to the ATP content of the water sample (APHA 1980). The method is simple and relatively inexpensive, and the instrument is stable and reliable. The disadvantages of the procedure are, 1) it does not estimate the active degrading biomass, and 2) it does not distinguish between living forms, e.g., bacteria, zooplankton, algae, fungi or yeast.

The biomass of bacteria in various waters can also be estimated by measuring the amount of cellular bound LPS. With this technique, LPS, which is a component of the cell walls of all gram-negative bacteria including cyanophytes (blue-green algae), is quantified.

Limulus amebocyte lysate (an aqueous extract of the blood cells of the horseshoe crab) will clot in the presence of LPS. Experimental conditions can be controlled so that LAL will become turbid rather than clot. Turbidity is then proportional to the concentration of LPS. Both bound and free LPS occur in aquatic samples. The cellular bound LPS must be quantified to estimate bacterial biomass. Centrifugation is used to separate the free from the bound LPS (Watson and Hobbie 1979). The procedure is relatively simple, inexpensive and yields reproducible results.

The test can be used to estimate bacterial biomass since most bacteria in the aquatic environment are gram-negative. However, the procedure does not detect gram-positive bacteria which could be an important population component in certain aquatic environments. In addition, the method estimates blue-green algae biomass which can be an important planktonic component in lakes, reservoirs, and slow moving streams.

Microbial biomass may also be estimated using the epifluorescence technique. However, it is extremely time consuming to make enough measurements to calculate the bacterial biomass from cell numbers and size.

### Sediments

Microbial populations in sediments can be estimated using modification of the plate count method and the epifluorescence technique. The same advantages and disadvantages of each method apply to their sediment counterparts as previously described. Plate counts can be used to measure bacterial numbers by transferring a known quantity of sediment (10 grams) into a dilution bottle containing glass beads. The bottle is then shaken for 10 minutes in a reciprocating shaker. Dilutions are made and plated out as described for the SPC method (Clark 1965).

The following modification can be used to estimate bacterial numbers in sediments using the epifluorescence technique: The sediment sample is poured into a blender and 100 ml of prefiltered water is added. Prefiltered water is water which passed through a filter of 0.2 m pore size no more than 6-8 hours before use. The contents are mixed at high speed for 1 minute. An aliquot of 0.5 ml of the mixture is removed and directly counted.

## Active Degrading Population

As previously stated, all the above procedures are used as indices or measures of total biomass or population size. A possible procedure for measuring the active degrading population is to use standard plating procedures with the organic compound of interest as the sole carbon source. Though the procedure has many disadvantages as discussed below, there does not appear to be any simple practical means of determining the size of the microbial population actually doing the degrading.

Often one disadvantage of the plate count or other methods that use the pollutant of interest as the sole carbon source is a gross underestimation of the active population because:

1. The pollutant may be toxic at concentrations needed to produce growth.

2. An acclimation period which may be required is not adequately provided.

3. Often pollutants are degraded bacteriologically in an "assembly line," where essential prerequisites (extracellular enzymes, vitamins, cofactors, etc.) may not be produced in the test environment.

4. The environmental conditions (pH, temperature, etc.) of the test environment may not be suitable for growth of the active population.

In addition, there is a series of reactions where a substance is only oxidized in the presence of other organic substances which would not be provided in a sole source carbon media. However, if the above series of significant problems can be eliminated, any method which could accurately measure the active population would be vastly superior as it would measure only the population of interest.

It is often assumed that biological degradation is essentially bacterial degradation. However, some compounds may be significantly degraded by algae, fungi, etc., and if their population is large enough, they may have to be considered. If the fate and transport model being evaluated can accept such biological degradation rate constants, these data will also have to be acquired. The procedure for field measurements of biomass, cells, etc., must be the same as was used in determining the rate constants.

The measurement of algae, macroinvertebrates, zooplankton, and fish biomass are discussed in the Bioconcentration section of this report. Whether such measures of biomass are necessary for validating a model depends upon whether the model has provisions for such inputs and whether the compound being studied undergoes significant degradation by the communities. Methods to measure pH are presented in the Hydrolysis section of the report.

### Temperature

Biological degradation of organic compounds is simply biological mediation of standard chemical reactions. These reactions usually result in a release of energy which is then used by the organism. The $Q_{10}$'s of each biological degradation rate constant should be determined. This is a laboratory procedure and, since it is considered a chemical input parameter, procedures for developing $Q_{10}$ rates are not provided here.

Environmental temperature is, however, a measurement which must be made in the field during the testing of models. The temperature of interest is that of the biota during the degradation process. Since most aquatic life forms have no thermoregulatory mechanisms, they are considered to be at the same temperature as the surrounding water.

Temperature measurement methods are rather simple and may involve the use of thermometers or thermocouples. Instruments must be accurately calibrated and procedures for their use are found in APHA (1980). The sampling design for determining temperature depends upon the model and the aquatic environment being sampled. If a compartmental type of model is being used, the temperature input should be representative of the biomass temperature of that compartment.

When the range of temperatures detected within a compartment is great, consideration should be given to reducing compartment size. Temperature profiles of lakes and streams are useful in determining the size of compartments since the temperature of well mixed water is constant.

## NUTRIENTS

Satisfactory methods to analyze water samples for total phosphorus, ortho phosphorus, ammonia, nitrite-nitrate-nitrogen, and Kjeldahl-nitrogen can be found in methods for chemical analysis of water and wastes (U.S. EPA 1979) or (APHA 1980).

## DISSOLVED OXYGEN

Both membrane electrode and the Winkler methods and its modifications can be used to measure dissolved oxygen (U.S. EPA 1979, APHA 1980). The Winkler method is a titrimetric procedure based on the oxidizing property of dissolved oxygen, while the membrane electrode procedure is based on the rate of diffusion of molecular oxygen across a membrane.

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# HYDROLYSIS

As a result of a significant amount of fundamental research that has been applied to evaluations of hydrolysis of chemicals in the aquatic environment, the hydrolysis of organic chemicals in solution is probably the best understood environmental process.

Hydrolytic reactions involve the introduction of a hydroxyl group (OH-) into a substrate molecule with loss of a leaving group (x) (Mabey and Mill 1976, Wolfe et al. 1976) (cf: Eq. 1).

$$R - X + H_2O \rightarrow R - OH + H - X \qquad (1)$$

where R is usually an organic moiety, and X is a leaving group (e.g. alcaholate, halide, etc.). Hydrolysis usually results in products which are more water soluble than the parent compound; whether or not the hazard presented by the parent compound is moderated by hydrolysis is, of course, dependent on the properties, reactivity and toxicology of the products themselves. To assess the reactivity of compounds under hydrolytic conditions similar to those of Equation 1, the environmental factors of pH and temperature must be addressed (Wolfe et al. 1976) as well as the unique characteristics of the compound itself.

The rates of hydrolysis in streams will depend heavily on the pH of the stream. The kinetics of hydrolysis have been described by Mabey and Mill (1976), where the rate of hydrolysis ($R_{hyd}$) may be expressed as:

$$\frac{-dS}{dt} = R_{hyd}, = k_{obs} [S] = k_B \ [OH^-] \ [S] + k_A \ (S) \ (H^+) + k_N \ (H_2O) \ (S) \qquad (2)$$

where (S) = concentration of hydrolyzable pollutant, $k_B$ and $k_A$ are the rate constants of the base $[OH^-]$ and $(H^+)$ acid promoted hydrolyses respectively, and $k_N$ is the rate constant for the reaction of the chemical with water. The half-life of the pollutant is calculated from:

$$t_{1/2} = \frac{0.693}{k_{obs}} \qquad (3)$$

Since in aquatic systems the hydrolysis of an organic chemical will not affect the concentration of water (55.5 M), the term $k_N$ $[H_2O]$ is essentially constant and can be represented as a first order constant, $k_N$. From the autoprotolysis equilibrium expression, the concentration of hydroxyl ion $[OH^-]$, is:

$$[OH^-] = K_w/(H^+) \tag{4}$$

Equation 2 can then be rewritten:

$$k_{obs} = k_A\ [H^+] + k_N + k_B \frac{K_w}{[H^+]} \tag{5}$$

Thus, the hydrolysis rate constant of a chemical is dependent on the relative values of $k_A$, $k_B$ and $k_N$, and on the hydrogen ion concentration $[H^+]$.

The rate of substitution of the hydroxyl group (OH-) for the leaving group (-X) on a molecule will also vary over several orders of magnitude (pH and temperature held constant) for different classes of compounds (Mabey and Mill 1976) as well as for compounds in the same class but with different peripheral structures. Wolfe et al. (1978) found this to be the case with carbamate pesticides. The hydrolytic half-life varied dramatically with structure.

Three types of hydrolytic reactions have been outlined by Mabey and Mill (1976) as important when considering the hydrolysis of different classes of compounds. The relative importance of the three processes will vary for different classes of compounds. For instance, the $k_N$ term is often negligible for hydroysis of some esters, and hydrolysis rates may then be strongly pH dependent with a minimum hydrolysis rate at around pH 5 (Mabey and Mill 1976). Other esters and carbamates (Wolfe et al. 1978) show a pH independent behavior at moderate pH values due to a dominant $k_N$ process, but are acid or base catalyzed at pH values <4 or >8, respectively. Simple non-halogenated alkanes, however, appear to have pH independent hydrolysis rates up to pH ∿10, which is usually beyond environmental relevance.

Hence, knowledge of the hydrolytic capabilities of an aquatic ecosystem requires a knowledge of the characteristics of the compound being hydrolyzed, the pH of the water body and the temperature. Organic priority pollutants for which hydrolysis is a significant fate process are listed in Table 4-1.

## METHODS

The two environmental factors that unequivocally affect the rate of hydrolysis of organic chemicals are pH and temperature. Although some authors have suggested that metal ions or humic acids may catalyze hydrolysis reactions, sufficient evidence for the environmental relevance of these

TABLE 4-1. PRIORITY POLLUTANTS FOR WHICH HYDROLYSIS IS ESTIMATED TO BE AN IMPORTANT FATE PROCESS

Pesticides

Endosulfan and Endosulfan sulfate
Heptachlor

Halogenated Aliphatics

Bromomethane
Bis (chloromethyl) ether
Bis (2-chloroethoxy) methane

Source: Callahan et al. 1979.

processes is not available, and therefore will be omitted at this time. These factors, pH and temperature, may need to be quantified in the field if the compound being investigated undergoes hydrolysis in natural aquatic systems.

### pH

The pH of a solution is its hydrogen ion activity expressed as the logarithm of the reciprocal of the hydrogen ion activity in moles per liter at a given temperature. The pH of a solution should be measured electrometrically since colorimetric methods suffer from interferences due to color, turbidity, salinity, colloidal matter and various oxidants and reductants (U.S. EPA 1979). To obtain an average compartment pH value, when more than one pH value is measured per compartment, an investigator may convert the pH values to hydrogen ion ($H^+$) activity. Next, he would average the ($H^+$) activity and reconvert the average $H^+$ value to an average compartment value.

It is also important that pH be monitored over a 24-48 hr period to confirm stability. If pH proves to be unstable then it would be necessary to weight the pH value by the hydrolysis rate to reflect the shifting hydrolysis rates in the average pH value. This could be done by averaging the pseudo-first-order rate constants generated from model simulations based on continual sampling of pH values over a diurnal period, and adjusting the pH input value such that the model output would equal this average rate constant.

### pOH

The pOH of a solution can be determined by subtracting the pH value from 14. Mean pOH values should be determined in an anlogous manner as pH values described above.

### Temperature

Methods to describe temperature are outlined in the Biotransformation section. In addition, temperature changes over time may have to be considered as were pH changes.

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# PHOTOLYSIS

Photolysis is the process whereby light energy is used to alter organic and inorganic chemicals. This process is influenced by several factors. Two important factors are the spectral qualities and intensity of the light. The spectral characteristics indicate the range of energies available in the photons. The intensity measures the number of photons available at a given energy level (wavelength).

When the photon interacts with the molecule, the molecule may absorb the energy available. If the wavelength is greater than ∿450 nm the molecule will not generally have sufficient energy to cause bond rupture (Stern and Walker 1978). Wavelengths in the 300-450 nm range will (if absorbed) provide sufficient energy for the photolytic process (≅ 95 K cal/mole) (Sundstrom and Ruzo 1978). In water, the shorter wavelengths <300 nm are not available because of absorbtion by atmospheric ozone. Once excited by a photon, a molecule may lose the energy through fluorescence or phosphorescence or it may undergo oxidation, reduction, displacement, isomerization, elimination or substitution (Crosby 1976). The molecule may also transfer its energy to another molecule.

Several other factors may influence the photolytic process in aqueous media. These are pH, temperature, the concentration of the chemical being studied, other chemicals available to interact with the chemical being studied, and turbidity of the water.

Temperature has always been a controlling factor in chemical reactions and it may be important in photochemical reactions. Turbidity has both been called a limiting factor (Herbes et al. 1979) and an enhancing factor depending on the study reported (Miller and Zepp 1979). One researcher showed that it reduced the rate (Herbes et al. 1979) and another showed that although the longer wavelengths were absorbed by the water, the scattering effect on the shorter wavelengths (<400 nm) actually caused a greater number of photons to be available (Miller and Zepp 1979).

Many environmental measurements can be made that give an indication of the wavelengths and intensity of light available for photolysis. The latitude, longitude, altitude, cloud cover, ozone concentration, time of year (season), and time of day affect the spectrum, intensity and angle at which the light strikes the water (Baughman and Lassiter 1978, Stern and Walker 1978, and Zepp and Cline 1977). This affects the shorter wavelengths more than the longer ones since the shorter wavelengths are affected by ozone, atmospheric absorption, and scattering (Sundstrom and Ruzo 1978). The angle at which the light hits the water also influences the amount of light reflected by the surface. This in turn affects the amount of light available in the water to promote photolysis (Baughman and Lassiter 1978, Stern and Walker 1978, and Zepp and Cline 1977).

The surface water conditions (rough versus smooth) as well as suspended particulates, biota, pigments, DOC and other turbidity factors determine light penetration and what wavelengths are available to act on the chemical. Eddy diffusivity also determines how much of the dissolved substrate is present in the photic ozone. If the chemical is not brought to the surface it may never be exposed to the photolytic process. Water pH and the chemical's condition (sorbed to soil particle, dissolved, ionized, etc.) also affect the rate of photolysis.

If one is unable to measure (throughout the day) the actual spectral characteristics of the site with a submersible spectral radiometer, then it is essential that not only the above conditions be noted, but that an estimate of cloud cover and any other factors (e.g., tree cover) that would reduce the total light available be obtained so that an estimate of available light energy can be made from data for clear day sunlight data. Most of these parameters (date, latitude, longitude, time of day, altitude, temperature, percent cloudiness, general ozone concentrations) are available for most areas of the country from NOAA, USGS, and EPA (air monitoring group).

Because spectral characteristics change throughout the year, they must be measured at the time of evaluation. The spectral radiometer will measure how much energy is available at each wavelength at the surface of the water, or at any depth of interest, light flux may also be evaluated using actinometers.

The chemical characteristics that are used to indicate susceptibility to change (pH, chemical concentration, etc.) can be measured in a laboratory using samples taken in the field. Table 5-1 lists major environmental factors which influence photolysis while Table 5-2 lists priority organic pollutants for which photolysis is estimated to be an important fate process. For more information on photolysis the following references may be of use: Mabey et al. 1982, Tinsley 1979, Smith et al. 1977, Haque 1980, Stumm and Morgan 1981, and Mill et al. 1980.

## METHODS

### Latitude (degrees)

Using a USGS 7-1/2' or 15' map of the area in which you are working, list the latitude of your site.

### Longitude (degrees)

Using the same maps as used for latitude and altitude, find and record the longitude.

### TABLE 5-1. SUMMARY TABLE OF ENVIRONMENTAL FACTORS THAT INFLUENCE PHOTOLYSIS

1. Spectral Characteristics and Intensity
    - a) Determined by
        - 1) Latitude
        - 2) Longitude
        - 3) Altitude
        - 4) Angle of Sun
            - a) Time of Day
            - b) Time of Year
        - 5) Cloud Cover
2. Light Intensity as Measured by Spectral Radiometer/Actinometer
3. Absorption Characteristics of Water and Solutes (dissolved organic carbon)
4. Turbidity
    - a) Suspended sediment
    - b) Microflora and Fauna (partially indicated by chlorophyll levels)
5. Eddy diffusivity
6. Depth
7. pH

## Altitude (m)

Using the USGS map (7-1/2' or 15') of your site, find the elevation above (or below) sea level. Multiply that number (in feet) by 0.305 to get meters, and report the data in meters.

## Time of Day (24-hour time)

List time of day using military time (24-hour clock).

## Cloud Cover (tenths)

Use of a pyranograph to quantify the available solar radiation is suggested when photolysis is a significant fate process. Pyranographs measure direct and incident sunlight in Cal/cm$^2$. Relative radiation on a daily basis can be estimated from comparison of daily pyranograph curves. Estimates of total daily radiation in Cal/cm$^2$ can be determined by cutting out and weighing the area under the daily pyranograph curves. To convert from Cal/cm$^2$ to percent cloud cover one must determine total radiation on a cloudless day (maximum value on cloudless day = 0% cloud cover) and on a day with extremely heavy cloud cover (minimum value or 100% cloud cover). The daily baseline values

TABLE 5-2. PRIORITY ORGANIC POLLUTANTS FOR WHICH PHOTOLYSIS IS CONSIDERED AN IMPORTANT FATE PROCESS

Pesticides

DDE
Dieldrin
Isophorone

Monocyclic Aromatics

Nitrobenzene
2,4-Dinitrotoluene
2,6-Dinitrotoluene
Phenol
Pentachlorophenol
2-Nitrophenol
4-Nitrophenol
2,4-Dinitrophenol
2,4-Dimethylphenol (2,4-Xylenol)
p-Chloro-m-cresol
4,6-Dinitro-o-cresol

Nitrosamines

Dimethylnitrosamine
Diphenylnitrosamine
Di-n-Propylnitrosamine

Polycyclic Aromatic Hydrocarbons

Acenaphthene
Acenaphthylene
Anthracene
Benzo [a] Anthracene
Benzo [b] Fluoranthene
Benzo [k] Fluoranthene
Benzo [g,h,i] Phylene
Benzo [a] Pyrene
Chrysene
Dibenzo [a,h] Anthracene
Fluoranthene
Fluorene
Indeno [1,2,3-cd] Pyrene
Naphthalene
Phenanthrene
Pyrene

Source: Callahan et al. 1979.

can be established by subtracting the minimum value from all other observations. By proportioning the daily baseline values to the maximum value, daily percent cloud cover can be determined.

Additional research is needed to establish representative minimum and maximum values. Research is also needed to determine if a linear function is appropriate between extremes. Even with the above constraints, this method is felt to be superior to the subjective estimates based on visual observations of an untrained observer. If a NOAA weather station is near the study site, and weather patterns for the site and the NOAA facility are similar, NOAA percent cloud cover estimates could be used.

## Light Intensity Measurements

Light intensity measurements may be made in several ways, and will depend on equipment or analytical instruments available as well as the time period of interest for the validation effort. For short term validations (few hours) a spectral radiometer or an actinometer system is suitable; for efforts of several days, actinometer systems are more practical. The use of actinometers is often preferable because the measurements take into account sunlight variations over a period of time (hours and days), while the radiometer method provides instantaneous light intensity readings at specific wavelengths. These methods are presently being further evaluated, and their relative capabilities are illustrated in Table 5-3.

TABLE 5-3. COMPARISON OF DIRECT MEASUREMENT TECHNIQUES AND SPECTRAL RADIOMETER METHODS

| Spectral Radiometer Method | Direct Measurement of $K_T$ |
|---|---|
| Moderately difficult, requires equipment (> $10K), calibration, expertise, power source at site, and probably two persons | Easy to do; requires chemicals and standard analytical equipment |
| Applicable to all compounds if uv spectra data available | Strictly applicable to chemicals of similar spectra |
| Practical limits on depth due to probe length in some units, other units are submersible | Usable for all depths |
| Obtains K values at discrete λ | Obtains integrated K value over λ and light intensity variations |
| Use of method more difficult over long time periods (time used to collect data and calculate K) | No problem with time period if chemical half-life is relevant to study[a] |
| Fundamentally sound method | Experimental development needed to assess limits |

[a] Use of a meter gives instantaneous light reading, which must then be integrated over time, but not wavelength.

Source: Mabey (Personnel communication)

Spectral Radiometer Measurements--

Use a spectral radiometer to measure light intensity at specific wavelengths, $\lambda$, at which absorption coefficients of chemical and natural water are measured; wavelengths described by Zepp and Cline (1977) or Mabey et al. (1982) are suitable. The amount of data obtained in the field measurement effort is in part determined by the intended use of the data and the model being validated.

EXAMS, for example, will accept the spectral radiometer readings taken when the sun is at its highest point or will accept a rate constant developed in the field or from its SOLAR program. At the present time, so many new electronic devices for measuring solar energy are available or in development, that anyone preparing to validate a model using a photolytically active chemical should carefully investigate the new products available.

Actionometer Measurements--

An actinometer should be a photo-reactive chemical whose chemistry is well understood. Rate constants as a function of seasons, latitude, and time of day should be known. The present state-of-knowledge allows such values to be estimated from absorption coefficients and reaction quantum yields for an actinometer at clear, cloudless sky conditions.

For its simplest use in a field study, the actinometer is exposed to sunlight under field conditions. The actinometer should be used in an area free of shadows, and with a non-reflecting background. If possible the photolysis rate of the actinometer should be chosen to approximate that of the chemical under study. The first-order rate constant for photolysis of actinometer [A] is the calculated from a plot of ln A vs T, and is designated $k_p^a$ (measured). The ratio of $k_p^a$ (measured) to the rate constant estimated for photolysis of actinometer under clear sky conditions then gives a correction factor that can be used to adjust any photolysis (or possibly abiotic oxidation rate constant) from clear-sky conditions to field sunlight conditions. One actinometer solution suitable for field use has been described by Mill et al. (1981), and its use is presently under final development.

## Dissolved Organic Carbon (mg/l)

In order to measure for dissolved organic carbon (DOC) in a water sample, it is first necessary to filter the sample using glass-fiber filter discs, to remove nonfilterable residue. Methods and materials for this filtering procedure are outlined in APHA (1980). The filtered sample is then analyzed using an infrared analyzer for total organic carbon (APHA 1980).

Water samples for DOC analyses should be collected and stored in glass bottles, preferably brown, and sealed with a teflon-lined cap. Samples should be analyzed promptly, but if delay is unavoidable, store samples at ice temperature with minimal exposure to light and atmosphere and acidify with hydrochloric acid to a pH not over 2 (APHA 1980).

## Suspended Sediment (mg/l)

See methods section in Physical Transport.

## Chlorophyll (mg/l)

The attenuation of irradiance in natural waters is a result from absorption of light by the water itself, green plants, dissolved organic matter, and suspended sediments. EXAMS relates absorption due to green plants to chlorophyll *a*, chlorophyll *b*, chlorophyll *c*, and phaeophytin *a*. Methods to determine the above pigments can be found in APHA (1980), and Weber (1973).

## Eddy Diffusivity ($m^2$/hr)

See methods section in Physical Transport.

## Depth (meters)

See methods section of Physical Transport.

## pH (in pH units)

See methods section in Hydrolysis.

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# OXIDATION

Three different mechanisms can be identified for the oxidation of organic contaminants in water:

1. Photooxidation
2. Chemical oxidation
3. Microbial oxidation

Actually, oxidation is the common end point of all the above processes. They differ only in the initiation mechanisms. Both photooxidation and microbial oxidation are discussed in other sections and will only be mentioned here with respect to their relationship to oxidation.

Photooxidation is an oxidation process which begins with the absorption of a photon of light energy by a molecule, raising it to an excited electronic state. It is this excited electronic state which subsequently gives rise either directly or indirectly to the oxidized species. Photooxidation is the major source of oxidant production.

Oxidation processes are dependent on several factors. Some of these factors appear to be the rate that oxygen dissolves, the concentration of oxygen, and the homogeneity of the dissolved oxygen in the water. These factors depend variously on meteorological conditions and surface and subsurface characteristics of the water body under investigation. Factors such as wind speed and surface turbulence play an important role in the dissolution rate of oxygen (Rathbun 1977; Holley 1978).

The temperature of the river will also have an effect on the rate of oxidation of an organic contaminant. This is true not only of chemical oxidation but also when metabolic function associated with microbial oxidation is considered. Microbial oxidation is initiated by enzymatic or metabolic processes which essentially predispose the pollutant molecule to oxidation. As the temperature of the water decreases, microbial activity decreases until it eventually becomes negligible. Therefore, season of the year as well as geographical location must be considered.

The production of oxidants by means of photooxidation is one mode of oxidation of organic contaminants. Photo production of oxidants such as singlet oxygen, alkyl peroxyl, or hydroxyl radicals are dependent upon such factors as the intensity and distribution of incident radiation, humic substances, and water temperature. Organic priority pollutants for which oxidation is estimated to be an important fate process are listed in Table 6-1. More specific information on oxidation is available in Mabey et al. 1982, Tinsley 1979, Smith et al. 1977, Haque 1980, and Stumm and Morgan 1981, Mill et al. 1980.

TABLE 6-1. ORGANIC PRIORITY POLLUTANTS FOR WHICH OXIDATION IS EXPECTED TO BE AN IMPORTANT FATE PROCESS

| |
|---|
| Monocyclic Aromatics |
| Phenol |
| Nitrosamines |
| Benzidine |
| 3,3'-Dichlorobenzidine |

Source: Callahan et al. 1979.

## METHODS

### Dissolved Organic Carbon

Methods to measure dissolved organic carbon are described in the Photolysis section.

### Free Radical Oxidants

The determination of the average steady-state free radical oxidant concentration in the natural water would be conducted in a manner similar to the singlet oxygen, except that cumene would be used as the probe chemical instead of DMF. Cumene is the suggested probe since reaction with free radical oxidants is the most important abiotic transformation process, and has been used as the probe chemical for such oxidations in aquatic systems (Mill et al. 1980).

### Oxidant Concentration

Standard methods for the determination of oxidant concentration in aqueous media have not been developed. The state-of-knowledge for oxidation process leaves no alternative except to employ research methods which directly estimate free radical oxidants or singlet oxygen present in natural waters. These measurements of oxidant concentration need only be performed when the rate of oxidation becomes a significant factor in chemical breakdown.

### Reaeration Rate

Methods to measure reaeration rates are described in the Volatilization section.

## Singlet Oxygen

Singlet oxygen concentrations in natural waters can be determined by reactions of a chemical known to only undergo reaction with singlet oxygen; Zepp et al. (1978) have used dimethyl furan (DMF), as a probe chemical. In the proposed method, DMF would be dissolved in a sterilized solution of natural water, and photolyzed in sunlight during the field study. The solution would be monitored for loss of DMF, and the concentration versus time data would be used to determine the first order rate constant for DMF loss. This rate constant would be divided by the known rate constant value for reaction of DMF with singlet oxygen. This ratio is then the average steady-state concentration of singlet oxygen for the duration of the experiment, and could be used in the computer model.

In addition, Zepp et al. (1981) suggest an approach for correlating singlet oxygen reaction rate constants with total organic carbon concentrations in natural waters.

## Suspended Particulate

Methods to measure suspended particulates are found in the Physical Transport section.

## Temperature and Dissolved Oxygen

Methods for temperature and dissolved oxygen are described in the Biotransformation section.

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# IONIZATION

The type of ion population characteristic of a lotic water body may directly influence the state of an added chemical contaminant. The extent to which the monovalent ($C^+,A^-$) and divalent ($C^{++},A^=$) ion population may ionize neighboring atoms and molecules (the ionization potential, H) depends on the amount of energy required to displace an electron on a neighboring atom or molecule (Morrison and Boyd 1973) and may be expressed by the following equation 1a.

$$A \rightleftarrows A^+ + E^- \quad = \quad H \tag{1a}$$

Similarly, dissociation may be expressed by equation 1b.

$$A - B \rightleftarrows A^+ + B^- \tag{1b}$$

The equilibrium between the ionized and un-ionized forms of a chemical species may be represented by the ionization constant ($K_i$), where (referring to equation 1a):

$$K_i = \frac{(A^+)(E^-)}{(A)} \tag{2}$$

Increases in entropy resulting from temperature increases, increases or decreases in pH, substitution of divalent for monovalent ions and vice versa (increase or decrease in electrostatic forces) or an addition of high-molecular-weight compounds, may influence the ionization potential and hence the equilibrium (Stumm and Morgan 1970).

However, not all molecules are affected similarly with respect to the effect of temperature on ionization. The influence of temperature upon ionization of water, carbon dioxide, and acetic acid reported by Stumm and Morgan (1970) showed large increases, slow increases, and a Maxwell-Boltzmann distribution of increase, respectively.

The pH of a solution may also characterize the ionization potential of a solution. For every acid or base there exists an acid dissociation ($K_a$) or base dissociation ($K_b$) constant determined from the following equilibria:

$$HA + H_2O \rightleftarrows H_3O^+ + A^- \tag{3}$$

$$K_a = \frac{(H_3O^+)(A^-)}{(HA)} \tag{4}$$

(Note: In equation 4, ($H_2O$) is incorporated in $K_a$).

$$B + H_2O \leftrightarrows HB^+ + OH^- \tag{5}$$

$$K_b = \frac{(HB^+)(OH^-)}{(B)} \tag{6}$$

(Note: In equation 6, ($H_2O$) is incorporated in $K_b$).

Since $K_a$ and $K_b$ (equations 4 and 6) represent the ratio of ionized to un-ionized species, the larger $K_a$ (or $K_b$), the greater the ionization potential of the system (Morrison and Boyd 1973). Temperature increases or decreases will affect this relationship according to the resultant entropy change.

In addition to the influence of pH and temperature on ionization, the total dissolved solids will give an estimate of both the un-ionized and ionized species and their concentration in the stream (Reid 1961). Specific conductance (conductivity) is commonly used to estimate the total dissolved solids (Reid 1961).

Modern procedures may include a species specific analysis. Some of the more common cations (calcium, magnesium, sodium, and potassium) and anions (sulfate, chloride, fluoride, nitrate, carbonate, and bicarbonate) found in streams characterize the stream's ion population. Other common ion species may include arsenic, barium, boron, bromine, chromium, copper, iodine, iron, lead, manganese, phosphate, selenium, silicon, strontium, and zinc (Hem 1970).

Water also self-protonates according to the following:

$$H_2O + H_2O \leftrightarrows H_3O^+ + OH^- \tag{7}$$

This must be considered (especially in dilute solutions) as a process which may alter the dissociation of any acid or base with a $pK_a$ comparable to that of water (Stumm and Morgan 1970). Equilibria of ionized and un-ionized species may also depend on the particular characteristics of the ionized form of a chemical. A selectivity coefficient Q of the form:

$$Q\ (Na_2R \rightarrow KR) = \frac{X_K\ R\ (NA^+)}{X_{Na}\ R\ (K^+)} \qquad (8)$$

or for second order reactions:

$$Q\ (Na_2R \rightarrow CaR) = \frac{X_{Ca}\ R\ (Na^+)^2}{X^2Na\ R\ (Ca\ ^{++})} \qquad (9)$$

can tell us whether sodium tends to bind with either calcium or potassium. These coefficients represent the equilibria for an interchange of ions but may not be constant (Stumm and Morgan 1970).

A compound may not reside in the water column but may precipitate into the sediment. If this happens, the cation anion composition may further determine the fate of the compound (Stumm and Morgan 1970). The substitution of less hydrated $Ca^{++}$ or $Mg^{++}$ by strongly hydrated $Na^+$ will result in swelling of the sediment and a reduced permeability (Stumm and Morgan 1970). As a result, transport through the interstitial waters will depend upon the hydration tendency of ionic species in the sediment, the elasticity of interlayer forces (which allow different interlayer spacing to develop), and factors influencing osmotic control, electrostatic force, and van der Waals forces. The process of ionization, however, is not limited to specific ion interaction or selfprotolysis, but augments its potential as an environmental process through the formation of colloidal suspensions.

Two classes of colloids exist: those which are hydrophobic and those which are hydrophilic (Stumm and Morgan 1970). The metal sols, such as silver halides and nonhydrated metal oxides are typical hydrophobic sols, whereas gelatin, starch, proteins, hydrated compounds and biocolloids (viruses-bacteria) are hydrophilic (Stumm and Morgan 1970). The ion exchange structure of these colloidal suspensions depends on interlayer attractions and lattice forces. The elasticity of attraction increases with organic content (Stumm and Morgan 1970). Addition of an ion with unmatched charge to a parent colloid may result in alterations of the parent colloid's surface chemical behavior. The fluctation of ionized species is primarily related to the charge and concentration of the ions in solution. The stability of the colloid depends exponentially on the relative magnitude of its energy barrier and can be represented by the equation:

$$W = \frac{K^{-1}}{2a^{e}}\ e\ \ Vmax/kT \qquad (10)$$

where: W is an indicator of stability; $k^{-1}/a$ is the ratio of the double layer thickness (the distance characterizing the repulsive interaction) to particle radius, k (the Boltzman constant); and T (temperature) represents the energy of attraction (Stumm and Morgan 1970).

If Vmax (the energy barrier) exceeds a value less than 15 kT, relatively stable colloids will be found. For example if Vmax $\geq$ 15 kT only 1 out of $10^6$ collisions will be successful (Stumm and Morgan 1970).

Colloidal destabilization can be accomplished by reducing $k^{-1}$ or increasing the concentration of electrolytes (unless aggregate size increases). This physical theory (a combination of van der Waals attractional forces and the repulsion of the Gouy-Chapman double-layers) has provided an analytical basis for the valency rule of Shulze and Hardy (Stumm and Morgan 1970). This rule simply states that the critical coagulation concentration (CCC) varies for mono-, di-, and trivalent compounds proportional to the ratio of $(6/z)^6$ (z represents ion valence) or 100:1.6:0.13. The rule is not applicable to metal oxide sols. Although the influence of aggregate size, and ion valency contribution, on stability may be complex; as a rule increasing stability is observed with increasing aggregate particle radius (Stumm & Morgan 1970).

Seasonal variation in runoff or the geochemical characteristics will determine the relative concentration, composition and longitudinal dispersal of the total dissolved solid present in the stream (Reid 1961). The physiography related to arid or humid plains, mountains, and valleys may determine the ionized and un-ionized species present. Reid (1961) characterizes those rivers with their headwaters in semi-arid plains as high in sodium, sulfate, and chloride but low in calcium and carbonate. Other examples include: rivers draining extensive plains in humid or temperate regions are characteristically high in sulfate and carbonate concentrations, but valley streams originating in granitic mountain regions show increased total dissolved solids. Youthful granitic mountainous region streams show high silica content and relatively low total dissolved solids (Reid 1961).

In summary, the ionized and un-ionized species in streams will contribute to the process of ionization if one or more of the environmental factors listed in Table 7-1 is changed. Whether the pH, temperature, total dissolved solids, or ionic strength vary may depend on geochemical characteristics inherent to the stream or the ionization capability of an anthropogenic chemical.

TABLE 7-1. ENVIRONMENTAL FACTORS THAT INFLUENCE IONIZATION OF ORGANIC COMPOUNDS IN WATER

| |
|---|
| Temperature |
| pH |
| Ionic Strength |
| Total Dissolved Solids |

## METHODS

### Temperature

Methods for temperature are described in the Biotransformation section.

### pH

Method for pH determinations are described in the Hydrolysis section.

### Ionic Strength

No standard method exists for direct determination of ionic strength; however, it may be indirectly determined via conductivity measurements (APHA 1980).

### Total Dissolved Solids

Methods for total dissolved solids may be found in Standard Methods (APHA 1980).

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# VOLATILIZATION

Volatilization of a chemical that is dissolved in water is the transport of the chemical from the water body to the atmosphere. The volatilization of organic substancees from aquatic environments to the atmosphere can be a significant environmental pathway, by which compounds are transported over wide areas. Volatilization rates are dependent on the vapor pressure of the chemical and the environmental factors that influence the movement to and from the evaporative surface. The pressure exerted by equilibrium vapor is known as the vapor pressure and is temperature dependent. Vapor pressures provide relative indications of the tendency of solutes to vaporize under unperturbed conditions (laboratory conditions). However, volatilization from a water solution is influenced by many environmental factors that tend to reduce the effective vapor pressure from the vapor pressure of a solute in distilled water under equilibrium conditions.

In moving from the bulk of the water to the atmosphere, a contaminant experiences three diffusive (transport) processes, each with a resistance. Normally, one of the three resistances will dominate. The resistance approach has been utilized to quantify contaminant movement from the water to the air (Mackay and Leinonen 1975, Mackay and Yuen 1980). The three diffusive resistances are:

1. $r_1$ = Resistance to diffusion from the bulk of the water to the interface,

2. $r_2$ = Resistance to diffusion through the near-surface liquid to the interface,

3. $r_3$ = Resistance to diffusion through the atmosphere in the layer close to the water surface.

The first resistance ($r_1$) is to that process needed to replenish the volatile compound in the top layer of water or to maintain an equal concentration of the pollutant throughout the water column. The process is normally sufficiently active, so that no concentration gradient of the pollutant will exist to retard the volatilization process. This resistance is thought to be important only in deep sluggish rivers or lakes and ponds. A knowledge of vertical mixing (eddy diffusivity) as a function of depth and time is required to understand the magnitude of this resistance in quiescent aquatic environments.

The second resistance ($r_2$) is referred to as liquid-phase resistance and represents the resistance to a molecule migrating from the near-surface water to the air-water interface. It is now generally accepted that turbulence in the near-surface region in the water phase controls the volatilization rate of highly volatile compounds in most rivers. Oxygen reaeration rates can be used as a measure of turbulence. The oxygen reaeration rate is the rate at which oxygen in the atmosphere dissolves in water that has a concentration of dissolved oxygen lower than the equilibrium concentration with the atmosphere (Mill et al. 1982). Oxygen reaeration rates of rivers have been correlated with river velocity, depth, and slope (Rathbun 1977, Mackay et al. 1982, Holley 1978). In general, turbulence increases with increasing velocity and slope and decreases with increasing depth.

Wind can also generate turbulence in near-surface layers. This effect, while generally minimal in lotic environments, is important in lentic environments. Cohen et al. (1978) demonstrated the importance of wind speed in laboratory wind-wave tests. They suggest that the prediction of liquid-phase resistance is best achieved by considering three wind-velocity ranges measured at 10 cm above the water column. At velocities below 3 m/s the effect of wind is negligible and liquid-phase resistance is strongly influenced by mixing originating from within the water body. In the second range, 3 to 10 m/s, liquid-phase resistance is basically controlled by wind-induced waves. Waves also increase the interfacial area, but since their height to length ratios do not normally exceed 0.143, this cannot account for more than a 4 percent increase in the transfer rate. Most environments have wind speeds in this region. In the third region, above 10 m/s, wave breaking may commence. A further decrease in liquid-phase resistance occurs in this region due to an increase in wave surface area, water spray, bubble entrainment and the disintegration of wave crests.

Solar radiation adsorption, direct heat transfer, and water evaporation may affect $r_2$. When surface waters are cooler than subsurface water layers, density gradients will tend to promote mixing and decrease $r_2$. Conversely, warm surface waters increase $r_2$ as they tend to stagnate and not mix with subsurface water layers (Mackay 1978).

The third resistance ($r_3$) is against diffusion through the surface layer to the atmosphere. Henry's constant, H, (the equilibrium partition coefficient expressed as vapor pressure divided by water solubility) and temperature basically control the process (Mackay and Yuen 1980). This resistance is relatively insensitive to temperature variations under normal environmental conditions since aqueous solubilities and mass transfer coefficients do not dramatically change. The magnitude of this resistance is inversely proportional to H and, therefore, compound dependent. For ionic compounds H is zero and no volatilization occurs (Mackay and Yuen 1980). Since aqueous solubility is one of the components of H, any environmental factor, e.g., pH and temperature, which can greatly influence solubility becomes important.

The total resistance $r_T$ is:

$$r_T = r_1 + r_2 + r_3$$

Most fate and transport models use the two-resistance ($r_2$ and $r_3$) or "two-film" concept to compute the export of chemicals across the air-water interface. The concept was originally developed by Whitman (1923) and has been successfully adapted to environmental problems by Liss (1973), Lin and Slater

(1974), and Mackay (1978). Most often, the resistance to mass transfer lies in these films. The other resistance ($r_1$) is often not considered in fate and transport models, e.g., chemical movement through a thermocline. Strong diel shifts in transport resistances in each phase of the air/water interface are possible. For example, volatilization of a nominally liquidphase resistance dominated compound can be retarded under still atmospheric conditions (Burns 1982).

Figure 8-1 is a logarithmic plot of vapor pressure versus aqueous solubility, with a number of compounds of environmental concern noted. Since H is vapor pressure divided by solubility, H is represented by solid diagonal lines. By locating the properties of a given compound an estimate can be made of its relative potential for volatilization. It is interesting to note that compounds of very low volatility such as DDT and PCB's will volatilize appreciably because of their low solubility. Hydrocarbons and halogenated hydrocarbons have a high volatilization potential while the more soluble organics, such as phenols, are less likely to volatilize (Mackay and Yuen 1980). The priority pollutants for which volatilization is thought to be an important process are listed in Table 8-1.

Henry's constants (H) are often determined in the laboratory using distilled water and the compound of concern. Predictions of volatilization based on "distilled water" chemical data are often high when applied to natural water where the pollutant is in low concentrations because of sorption of the compound to organic or mineral materials (Mackay 1978).

Table 8-2 lists the major environmental factors that influence volatilization rates. In addition, any process which tends to sequester, transform, or degrade the parent compound such as ionization, sorption, photolysis, microbial degradation/transformation will obviously retard the volatilization rate of the parent compound.

Surface films impede transfer processes at the interface. This may be due either to a "blocking" effect or to a reduction of near-surface turbulence. When visible scums due to algal blooms or higher aquatic plants or slicks are present, the rate of volatilization will be reduced. Also, volatilization will be severely reduced or eliminated when a continuous ice cover is present (MacKay and Yuen 1980).

For additional information, the reader is referred to "Volatilization of Organic Pollutants from Water" by Mackay et al. (1982). The report elucidates factors which control volatilization, and develops methods for calculating rates. Also, it contains theoretical and experimental studies and a comprehensive review of the equilibrium physical chemistry and thermodynamics of systems involving hydrophobic organic solutes and water.

## METHODS

The input parameters necessary for volatilization include pH and temperature (°K), compartment dimensions, area and volume, and mixing. Parameters necessary as input to mixing are eddy diffusivity, the reaeration rate of the

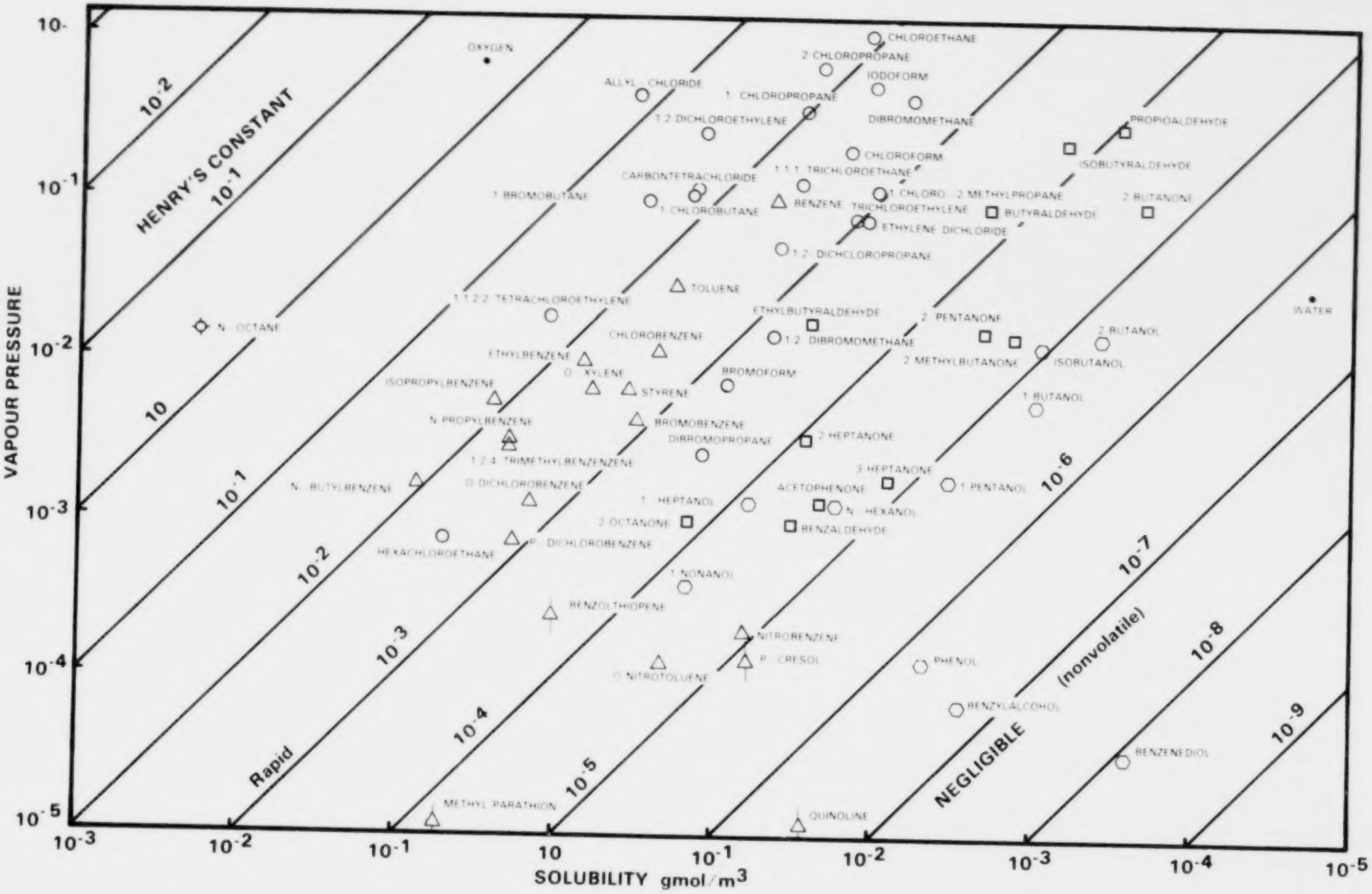

Figure 8-1. Plot of solubility, vapor pressure, and Henry's Constant depicting relative volatilization rates (modified from Mackay and Yuen 1980).

TABLE 8-1. ORGANIC PRIORITY POLLUTANTS FOR WHICH VOLATILIZATION IS ESTIMATED TO BE AN IMPORTANT TRANSPORT PROCESS

Halogenated Aliphatics

Chloromethane (methyl chloride)
Dichloromethane (methylene chloride)
Trichloromethane (chloroform)
Tetrachloromethane (carbon tetrachloride)
Chloroethane (ethyl chloride)
1,1-Dichloroethane (ethylidine chloride)
1,2-Dichloroethane (ethylene dichloride)
1,1,1-Trichloroethane (methyl chloroform
1,1,2-Trichloroethane
1,1,2,2,-Tetrachloroethane
Chloroethane (Vinyl chloride)
1,1-Dichloroethane (Vinylidine chloride)
1,2-trans-Dichloroethane
Trichloroethane
1,3-Dichloropropane

Bromomethane
Dichlorodifluoromethane
Trichlorofluoromethane

Ethers

2-Chloroethyl vinyl ether

Monocyclic Aromatics

Benzene
Chlorobenzene
1,2-Dichlorobenzene (O-Dichlorobenzene)
1,3-Dichlorobenzene (m-Dichlorobenzene)
1,4-Dichlorobenzene (p-Dichlorobenzene)
1,2,4-Trichlorobenzene
Ethyl benzene
Toluene

Pesticides

DDD
DDE
DDT
Dieldrin

Source: Callahan et al. 1979.

TABLE 8-2. ENVIRONMENTAL FACTORS THAT INFLUENCE VOLATILIZATION RATES

pH
Temperature

Mixing
  Eddy Diffusivity
  Reaeration Rate
    Wind Speed
    Slope
    Water Velocity

compound, wind speed near the water surface, slope of the river, and water velocity.

### pH

The measurement of pH is described in the methods section of Hydrolysis.

### Temperature

Procedures for measuring water temperature are described in the methods section of Biotransformation.

### Compartment Dimensions, Area and Volume

Procedures for determining compartment dimensions, area and volume are described in the methods section of Physical Transport.

### Mixing

Parameters necessary as input to mixing are eddy diffusivity, reaeration rate, wind (speed), slope (of river surface) and water velocity.

1. Eddy Diffusivity. For determining eddy diffusivity refer to the methods section of Physical Transport.

2. Reaeration Rate. The reaeration rate can be measured directly but this is not often possible because of the specialized equipment and time required. Rathbun and Grant (1978) have developed a technique using ethylene or propane as indicators of volatilization and Rhodamine WT dye as an indicator of dispersion and dilution. This method provides a direct measure of volatilization of compounds with high H (Henry's constant) values. In addition, reaeration rates can be estimated in the field by measuring the rate of oxygen release from the water into a nitrogen-purged dome (Copeland and Duffer 1964, Hall 1970).

   Where direct measure is not possible, the reaeration rate for a specific site can be computed based on a knowledge of the physical characteristics of the site. McKay and Yuen (1980) presented several equations for calculating the reaeration rate for oxygen in streams:

   Tsivoglou and Wallace (1972) $K_2 = 638VS$

   Parkhurst and Pomeroy (1972) $K_2 = 1.08\ (1.0 + 0.17F^2)(VS)0.375Z^{-1}$

   Churchill et al. (1962) $K_2 = 0.00102V^{2.695}Z^{-3.085}\ S^{-0.823}$

   where S is the river slope (m/m), Z average depth (m), V velocity (m/s), and F the Froude Number $V/(gZ)^{0.5}$ (g=gravitational force)

If no slope data are available the following equations can be used:

Isaacs and Gaudy (1968) $K_2 = 0.223VZ^{-1.5}$

Langbein and Durum (1967) $K_2 = 0.241VZ^{-1.33}$

Mackay and Yuen (1980) state that, for a given river it is likely that these equations would give an estimate of $K_2$ with an average error between 10 and 50 percent. They suggest that one approach may be to apply all the equations, discard the outlying results and take an average of the remainder.

Reaeration may be primarily determined by local winds in lakes and ponds. The effect of windspeed on reaeration rates can be separated into two distinct zones as described by Banks (1975) and Banks and Herrera (1977). At windspeeds (at 10 m height) greater than about 5.5 m/s the exchange constant increases as the square of the wind velocity. At windspeeds of less than about 5.5 m/s exchange constants correlate with the square root of windspeed. Banks (1975) presents the following oxygen exchange equations:

$$KL = 3.2 \times 10^{-7}\ U^2 \quad (U > 5.5\ m/s)$$

$$KL = 4.19 \times 10^{-6} \sqrt{U} \quad (U < 5.5\ m/s)$$

where

KL = oxygen exchange constant (m/s)

U = windspeed (m/s) at 10 m above the water surface.

Finally, Smith et al. (1977) have presented the following depth-dependent ranges and "suggested values" for oxygen reaeration rates for various water bodies:

| | Range ($hour^{-1}$) | ($hour^{-1}$) |
|---|---|---|
| Pond | 0.0046-0.0096 | 0.008 |
| River | 0.0042-0.39 | 0.04 |
| Lake | 0.004 -0.013 | 0.01 |

3. Wind. The influence of wind upon mixing is greatest for lakes and ponds and less important for rivers. In many cases, weather station data may suffice. Wind speeds recorded at a given height can be converted to EXAMS input values (wind velocity at 10 cm above the water surface) by the assumption of a logarithmic wind profile

(Israelsen and Hansen 1962). The following equation describes the relationship:

$$V_1/V_2 = \log\left(Z_1/Z_o\right) / \log\left(Z_2/Z_o\right)$$

where:

$V_1$ = Windspeed in m/s at height $Z_1$ in $\mathrm{mm}_1$

$V_2$ = Windspeed in m/s at height $Z_2$ in $\mathrm{mm}_1$

$Z_o$ = Effective roughness height in mm. The roughness height is generally on the order of one millimeter over water bodies.

When weather stations are not sufficiently close to the water body of interest, or if an investigator deems that greater accuracy is required, direct field measurements may be taken as follows. Wind speed should be measured in close proximity (shoreline) to the waterbody of interest or above the water surface. Units should be measured in or converted to m/sec. The anemometer chosen should be capable of measuring wind speed below 3 m/sec, as this is an important value with respect to liquid phase diffusion. For information on anemometer types, consult U.S.G.S. (1977).

4. Slope. The slope (of water surface) of a particular stream section can be determined using elevations from U.S.G.S. quad sheets. Units should be converted and reported in meters change in elevation/meters distance along stream.

5. Water Velocity. Procedures for measuring water velocity are described in the methods section of Physical Transport.

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# SORPTION

## PROCESS DESCRIPTION

The partitioning of compounds between water, sediments, and biota in aquatic systems can be an important process affecting pollutant fate. Sediments can act as a sink for sorbed chemicals, as they are removed from the water column or as a source at a later time when the chemicals are released (desorbed) from the sediments. When a solution containing a dissolved chemical contacts a solid surface sorption may occur. Normally when the total amount of chemical is increased in a system, the amount of chemical which is sorbed is also increased (Mill et al. 1982).

Sorption is defined as the binding process of chemicals to surfaces of solids through chemical or physical interactions or a combination of both. The process of adsorption implies only physical interaction of molecules of gases, dissolved substances or liquids to the surface of solid bodies. The term sorption will be used in this report so as not to exclude chemical mechanisms in the binding process.

A sorption-desorption phenomenon depends on the physical and chemical characteristics of the sorbate (chemical pollutant), sorbent (material that the chemical adheres to), and environmental conditions.

## CHARACTERISTICS OF THE SORBATE

The properties of the sorbate are key factors determining the sorption or partitioning of a chemical in the environment. Poinke and Chesters (1973) state that the basic distribution (partitioning) depends more on the physicochemical characteristics of the chemical than on the characteristics of the sorbent or environmental conditions. An excellent review of the properties that determine the role of the sorbate in sorption and desorption is provided by Bailey and White (1970). They conclude that the following properties of the sorbate molecule are important: 1) chemical character, shape, and configuration; 2) acidity or basicity; 3) water solubility; 4) charge distribution for organic cations; 5) polarity; 6) molecular size; and 7) polarizability.

Since the purpose of the report is to review the influence of environmental factors on fate and transport processes, the influence of the sorbate properties will not be presented in detail. However, the following represent important generalizations which were derived from the literature:

1) Organic molecules with a negative charge (anions) are unlikely to be sorbed to an appreciable extent (Knight et al. 1970, Alexander 1961);

2) Cationic compounds are sorbed to a greater extent than neutral molecules.

Their sorption can occur by cation exchange (Faust 1977, Baughman and Lassiter 1978);

3) Larger cations are sorbed more readily than smaller ones (Faust 1977);

4) With the exception of sorption by cation exchange, the most insoluble compounds (neutral) are the most strongly sorbed (Baughman and Lassiter 1978);

5) Neutral, hydrophobic compounds with high octanol/water partition coefficients are most likely to be sorbed (Karickhoff et al. 1979);

6) The sorption of hydrophobic compounds will be positively correlated to the organic carbon content of the sorbent (Karickhoff et al. 1979, Faust 1977, Poinke and Chesters 1973);

7) Desorption of many pesticides occurs at a much slower rate than sorption, e.g., simazine, atrazine, linuron, monuron, and aldrin (Faust 1977, Poinke and Chester 1973).

## CHARACTER OF THE SORBENT

The properties of the sorbent that influence sorption are primarily related to the area and configuration of the surface, and to the magnitude, distribution and intensity of the electrical field at the surface (Bailey and White 1970). In the aquatic environment a chemical can adhere to the surface of soil particles, clay minerals, colloids, (such as oxides and hydroxides of iron, aluminum and manganese), biotic organic matter such as phytoplankton, periphyton, higher aquatic plants, fish, insects, zooplankton, bacteria, and fungi, and other abiotic organic matter.

The sorption of most hydrophobic compounds is positively correlated with organic carbon content of the sorbent and less well with mineral content (Poinke and Chesters 1973). This results, in part, from 1) the high charge and large specific surface area associated with highly-decomposed organic matter, and 2) the fact that clay minerals form organo-clay complexes which can reduce the number of sorption sites available.

Another factor in the sorption of cation and hydrophobic compounds to sediments is the correlation of sorption to decreasing particle size (Baughman and Lassiter 1978, Karickhoff et al. 1979). Karickhoff et al. (1979) were able to show that the sorption behavior of hydrophobic pollutants can be estimated within a factor of two from a knowledge of particle size distribution and organic content of the sediment, and the octanol/water partition coefficient of the pollutant.

Sediment sorption of cation and hydrophobic organic compounds is strongest with fine particles because of the higher surface to volume ratio (Baughman and Lassiter 1978). Table 9-1 shows the effect of particle size on partition coefficients for hydrophobic chemicals (methoxychlor and pyrene) and cation exchange (paraquat).

TABLE 9-1. INFLUENCE OF PARTICLE SIZE ON PARTITION COEFFICIENTS

| Size Fraction | $K_{oc}$* Methoxychlor | $K_{oc}$* Pyrene | $K_p$** Paraquat |
|---|---|---|---|
| Sand | 22,000 | 19,000 | 400 |
| Coarse silt | 73,000 | 92,000 | 25,000 |
| Medium silt | 88,000 | 128,000 | 35,000 |
| Fine silt | 93,000 | 122,000 | 250,000 |
| Clay | 81,000 | 109,000 | 750,000 |

Source: Baughman and Lassiter (1978)

*$K_{oc}$ The amount of chemical sorbed per unit of organic carbon divided by the concentration of chemical in the water.

**$K_p$ The concentration of a pollutant in the sorbent divided by concentration of pollutant in the water at equilibrium.

While the sorption of nonpolar and polar neutral organic molecules is usually positively correlated with the organic carbon content of the sorbing solid, charged organic molecules often behave differently with their sorption more related to the clay mineral content. Two important properties of the mineral sorbent that control sorption are cation exchange capacity and surface area. Sorption of charged organic molecules will generally increase with an increase in the surface area and in the cation exchange capacity of the sorbent.

Biota play an important role in the distribution of organic compounds in the aquatic environment (Faust 1977). Poinke and Chesters (1973) point out that aquatic weeds can sorb significant quantities of organophosphorus and organochlorine pesticides in relation to the bottom sediments. For example, in one study the most rapid sorption and greatest concentration of p,p'-DDT was associated with vegetation and not the sediments (Bridges et al. 1963). Also, it should be noted that considerable quantities of organics can be sorbed by fish, insects, and zooplankton (Hamelink et al. 1977).

Sorption of a chemical to the sediments is basically limited to the upper exposed layers. Important physical factors influencing sediment sorption are the actual amount of sorbent (dry weight) per volume of sediment or conversely, the percent water content and bulk density of the sediment. If the sediment contains a high percentage of water and low bulk density, less material per volume of sediment will be available for sorption than if the sediment contained a low percentage of water and high bulk density per volume of sediment.

## ENVIRONMENTAL FACTORS INFLUENCING SORPTION

Besides the characteristics of the sorbate and sorbent, environmental conditions affect sorption phenomena. The major environmental factors that influence sorption are pH, temperature, biota, and the presence of other dissolved organics.

Since the ionization state of a chemical can greatly influence sorption, a knowledge of the pH of the water and sediment is important. The strength of sorbtion will depend on the degree of ionization particularly where the sorption mechanism is ion exchange.

Neutral compounds or strong acids or bases will not be affected by changes in pH, since their form is not dependent on the pH of their environment (Mill et al. 1982). Depending on the pH of the environment, weak acids or bases may be present in two different forms. Under low pH conditions, weak bases will be in the cationic form and weak acids in the free acid form. Since most sediments have negatively charged sites the free acid and cationic forms will be more highly sorbed than their respective anionic acid and free base counterparts. Therefore, as the pH of a sorption system decreases the sorption of weak acids and bases increases.

Since sorption processes are normally exothermic and desorption processes are endothermic, an increase in temperature would normally tend to reduce sorption and favor desorption (Bailey and White 1970). With increased temperatures attractive forces between solute and the solid surface are weakened, with a concomitant increase in solute concentration. Cationic pesticides that are sorbed to highly organic soils are normally not significantly influenced by temperature variations (Poinke and Chesters 1973).

Organic chemicals are generally sorbed less when other indigenous dissolved organic chemicals are present. This decrease in sorption is apparently due to two processes. First, the increased solubility of the organic chemical of interest in the presence of other organic materials, since sorption has been found to correlate inversely with solubility. The second process that results in decreased sorption is the competition for sorption sites. Naturally occuring organics will also be sorbed on sediments and any sorption will decrease the total number of sorption sites available to the chemical of interest (Mill et al. 1982).

Sorption of a chemical to bottom sediments is often limited to the upper exposed layers. However, bioturbation can increase the depth of the distribution of the chemical in the bottom sediments (Aller 1978, Rippey and Jewson 1982). Bioturbation may result in physical disturbance by demersal fishes, irrigation of sediments by tube-dwelling macrofauna, and mixing of contaminated layers by macrofauna populations after the contaminant has sorbed to the sediment surface. Benthic organisms may also affect partical size distribution and seasonal layering of sediment deposits by ingesting sediments in sub-surface layers and depositing fecal material at the surface (Davis 1974).

Table 9-2 lists the environmental factors, including the properties of the sorbent, which most influence sorption rates. Organic priority pollutants for which sorption is thought to be an important process in aquatic systems are listed in Table 9-3.

## METHODS

### General Considerations

Sorption is defined as the binding process of chemicals to surfaces of sediments through chemical and/or physical interactions. In the aquatic environment a chemical generally adheres to sediments, suspended particles, and biota. Sorption of nonpolar organic chemicals onto sediments is a function of the partition coefficient of the compound, the organic carbon and water content and bulk density of the sediment. Also, under certain conditions particle size may greatly influence sorption.

The partition coefficient of a chemical is measured by equilibrating an aqueous solution of the pollutant in an environmentally realistic concentration with a known concentration of sediment. After reaching equilibrium the distribution of chemical between the water and sediment phases is measured. The partition coefficient for a particular nonpolar compound can be normalized to the organic content of aquatic sediments. The normalized sorption constant ($K_{oc}$) is described by the following equation at equilibrium conditions:

$$K_{oc} = \frac{\dfrac{\text{Chemical sorbed to sediment/dry weight of sediment}}{\text{Water concentration of chemical}}}{\text{Percent organic carbon in sediment}} \times 100$$

$K_{oc}$ can be a stable, system-independent measure of an intrinsic property of nonpolar organic compounds. For a compartmentalized fate and transport model, $K_{oc}$ can be used to compute a partition coefficient for sediment phases of an aquatic system as a function of the organic carbon content of each sediment compartment. $K_{oc}$ is strongly correlated with the octanol-water partition coefficient ($K_{ow}$) (Karickhoff et al. 1979). By definition, $K_{ow}$ expresses the equilibrium concentration ratio of an organic chemical partitioned between octanol and water in a dilute solution. $K_{oc}$ can be estimated as 41 percent of $K_{ow}$ for whole sediments.

Sorbtion of a chemical to the sediments is basically limited to the upper exposed layers. An important factor influencing sediment sorption is the actual amount of sorbent (dry weight) per volume of sediment or conversely the percent water content and bulk density of the sediment. Therefore, if an investigator is given a $K_{oc}$ or $K_{ow}$ value as part of the chemical input data to a model, he would have only to describe the average organic carbon content, bulk density, and water content of each sediment compartment to estimate sediment sorption.

However, it is possible that in addition to organic carbon, sorption can be correlated with total amount of surface area of the sorbing material

## TABLE 9-2. ENVIRONMENTAL FACTORS AND SORBENT PROPERTIES WHICH MOST INFLUENCE SORPTION RATES

| Environmental Factors | Sorbent Properties |
|---|---|
| pH | Percent organic matter |
| Temperature | Particle size/surface area |
| Dissolved organic carbon | Percent water |
| Biota | Bulk density |
|  | Cation exchange capacity |

## TABLE 9-3. ORGANIC PRIORITY POLLUTANTS FOR WHICH SORPTION IS ESTIMATED TO BE AN IMPORTANT PROCESS

**Pesticides**

- Aldrin
- DDD
- DDE
- DDT
- Dieldrin
- Endosulfan and Endosulfan sulfate
- Heptachlor epoxide
- Hexachlorocyclohexane
- TCDD
- Toxaphene
- Polychlorinated biphenyls

**Polycyclic Aromatic Hydrocarbons**

- Acenaphthene
- Acenaphthylene
- Anthracene
- Benzo [a] Anthracene
- Benzo [b] fluoranthene
- Benzo [k] fluoranthene
- Benzo [g,h,i] perylene
- Benzo [a] pyrene
- Chrysene
- Dibenzo [a,h] anthracene
- Fluoranthene
- Fluorene
- Indeno [1,2,3-cd] pyrene
- Naphthalene
- Phenanthrene
- Pyrene

**Monocyclic Aromatics**

- Hexachlorobenzene
- 2,4-Dinitrotoluene
- 2,6-Dinitrotoluene
- Pentachlorophenol
- 2-Nitrophenol
- 4-Nitrophenol
- 2,4-Dinitrophenol
- 4,6-Dinitro-o-cresol

**Phthalate Esters**

- Dimethyl phthalate
- Diethyl phthalate
- Di-n-butyl phthalate
- Di-n-octyl phthalate
- Bis (2-ethylhexyl) phthalate
- Butyl benzyl phthalate

**Halogenated Aliphatics**

- Hexachlorobutadiene

**Nitrogen-containing Compounds**

- Benzidine
- 3,3-'Dichlorobenzidine
- 1,2-Diphenylhydrazine

Source: Callahan et al. 1979.

(particle size). Increased sediment sorption generally correlates to decreasing particle size (Baughman and Lassiter 1978). Particle size may be particularly important for sediments with an organic content so low that sorption to organic surfaces is insignificant compared to sorption by inorganic surfaces. In these instances particle size data may be required to accurately estimate sediment sorption. Further information on this topic is provided by Poinke and DeAngelis (1979).

Polar organic molecules also sorb to sediments, suspended particles, and biota. Sorption of polar molecules (ions) also correlates with organic carbon, but not as closely as do nonpolar ones. In general polar compounds often behave differently, and some property or combination of properties other than organic carbon may have to be used in the development of a normalized sorption constant for polar compounds. Possible factors that could be used in the development of a normalized sorption constant for polar compounds include cation exchange capacity, anion exchange capacity, particle size, and pH. The complexity of this process has hindered the development of robust, system-independent analogs of the Koc for nonpolar organics.

If the only chemical input data for sediment sorption is a partition coefficient, an investigator can apply it equally to all sediments or develop a partition coefficient which is specific for the chemical and site of interest.

As noted earlier, chemicals also adhere to suspended sediments and biota. To estimate sorption to suspended sediments, Koc or Kow constants can be applied if one knows the mass of suspended sediments and their percent organic carbon.

The actual quantities of a chemical captured by the biomass are often relatively small, compared to the amounts sorbed by sediments or dissolved in the water column. Therefore, biomass is often relatively insignificant as a transport or capture medium affecting the fate of an organic pollutant. However, biomass accumulation of pollutants is extremely important because of the possibility of direct toxic effects on aquatic life or the possibility of toxic effects on man through food-chain vectors. Also, biota may be an important factor in distribution of the contaminant via bioturbation.

A biomass partition coefficient (bioconcentration factor) may be provided as part of the chemical input data to a given model. This factor may apply to specific populations, e.g., fish, benthos, etc., or to functional groups (carnivores and herbivores) or the entire population. With this factor an investigator would need to measure the biomass of the appropriate population. Methods to measure biomass are described in the Bioconcentration section of this report.

### Sediment Sampling

To utilize normalized sorption coefficients in a compartmentalized fate and transport model, representative sediment samples are required. For example, the average percent organic carbon content of each sediment compartment would be a required input value if a $K_{oc}$ or $K_{ow}$ were provided. In addition, the volume of each sediment compartment would be needed. Length and width measurements of sediment compartments can be readily obtained from maps. However, what is an appropriate depth of a sediment compartment? Obviously, chemicals must be exposed to sediments before sorption can occur. Often, only the upper surface layers of sediment can participate in sorption phenomena. One possible solution to this problem is to take sediment core samples. The depth at which the chemical of interest can be detected can be used as the depth of the sediment compartment.

Sediments are largely eroded soils that have been subjected to redispersal and particle size fractionation. In the aquatic environment, dispersion of suspended particles follows sedimentation patterns. Sedimentation patterns are a function of particle size and density, and current velocities. Sediments in a given aquatic environment may be fairly uniform. For example, sediments in a river system may be distributed as follows: 1) clay suspended in the water column, 2) sand in the middle bottom sediments, and 3) silt at the edge of the stream. In a reservoir or lake environment coarser grained sediments are generally deposited near the headwaters of a reservoir/lake with the bed sediments near the center composed of fine grained materials. For sediment samples to be representative of a given compartment, sample allocation needs to be proportional to the geographical distribution of the various size fractions of the sediments. Methods for sediment collection are described in the Physical Transport section of this report.

## Sediment Analysis

An investigator may have to measure the following sediment properties for inputs to fate and transport models: total organic carbon content expressed as percent, anion exchange capacity, cation exchange capacity, pH, percent water content, bulk density, and particle size. In addition, one may need to measure suspended sediments and their percent organic carbon. Methods for determination of suspended sediments, bulk density, percent water, particle size, and total organic carbon content of bottom sediments are given in the Physical Transport section.

### pH of Sediments--

Sediment pH can be measured by a procedure described by Peech (1965). One part of a sediment is added to two parts of .01M $CaCl2$ to adjust the ionic strength of the suspension. The suspension is stirred several times over a 30-minute period and allowed to stand for 30 minutes to settle before measurement with a glass electrode. The glass electrode is immersed into the suspension, but the reference electrode remains in the clear supernatant above the suspension to minimize liquid junction potential effects.

### Cation Exchange Capacity--

Cation exchange in sediments is a reversible chemical reaction. Cations held on the surface and within sediments can be replaced with cations of salt solutions and acids. Cation exchange capacity (CEC) is defined as the sum of the exchangable cations of a sample (usually expressed as milliequivalents per 100 g of sample).

Many methods have been and continue to be proposed to determine CEC. Kelley (1968) and Peech (1965) describe in detail the pitfalls of various methods. The ammonium acetate and sodium acetate methods are often used as the "standards" for the comparison of new methods. The "standard" methods do not accurately reflect field conditions since the pH and ionic strength of the test medium (important factors affecting CEC) are altered in the analytical procedures. The sodium and ammonia methods are described by Black et al. (1965).

### Anion Exchange Capacity--

The anion exchange reaction of sediments may be described as the substitution of one anion by another which is available in solution in a greater concentration or possesses a stronger tendency to hold its position on the sediment. The anion exchange capacity (AEC) of a sediment is measured by the amount of an anion sorbed and then displaced from a sediment. Phosphate or arsenate anions are frequently used to measure AEC. Dean and Rubins (1947) described methods to measure AEC.

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# BIOCONCENTRATION

## INTRODUCTION

The characteristic of living organisms to act as compositors and integrators of toxic substances from the environment is well known. Aquatic organisms concentrate and accumulate substances directly from the water and through the food chain (Rudd 1964; Woodwell et al. 1967). Uptake of toxic substances is not restricted to aquatic organisms directly in contact with the water. This is illustrated by thinning of egg shells and reproductive failure of birds that prey upon fish contaminated with DDT and its derivatives (Hickey and Anderson 1968; Anderson and Hickey 1970), and reproductive difficulties of commercially raised mink that were fed Lake Michigan coho salmon (40 percent of their diet) contaminated with PCBs (Metcalf 1977).

Three processes are involved in biological uptake of toxic substances: bioconcentration, bioaccumulation, and biomagnification. The terminology of the three processes is clarified by Brungs and Mount (1978) as follows: "Bioconcentration is usually considered to be that process by which toxic substances enter aquatic organisms, by gill or epithelial tissue, from the water. Bioaccumulation is a broader term in the sense that it usually includes not only bioconcentration but also any uptake of toxic substances through consumption of one organism. Biomagnification refers to the resultant total process including bioconcentration and bioaccumlation by which tissue concentration of bioaccumulated toxic substances increases as this material passes up through two or more trophic levels."

## UPTAKE RATES AND MECHANISMS

A number of factors influence uptake of organic constituents from the water and through the food chain, but there is a lack of agreement among investigators regarding the significance of various factors. Hamelink et al. (1977) list the primary factors governing the quantity of residues available directly from the water as the concentration of the compound in the water, the volume of water passed over the gills and the efficiency with which fish extract the compound from the water. Metcalf (1977) points out that absorption of lipid soluble substances from water is a function of the concentration of compound times the exposure time. Several investigators have noted direct relationships between residue concentration in tissues of fish and the age or size of the animal. Hamelink et al. (1977) suggested that the rate at which DDE and mercury are acquired from both food and water by fish versus their growth rate may largely determine residue concentrations. Metcalf (1977) observed that bioconcentration of DDT and dieldrin by fish from coldwater lakes is essentially a linear function of the age of the fish. Youngs et al. (1972) reported that concentrations of DDT residues and its metabolites increased with the age of lake trout (Salvelinus namaycush) from Cayuga Lake, New York. Reinert (1970) reported that concentrations of DDT and dieldrin increased steadily with the size of Lake Michigan lake trout. Residue concentrations may also vary among species of fish (Reinert 1970), suggesting that feeding habits, distribution patterns, physiological characteristics, life cycles, fat content and other species-specific factors influence bioaccumulation rates.

DeFoe et al. (1978) noted that female fathead minnows accumulated about twice as much PCBs as males exposed to similar concentrations in water, presumably because of the greater amount of lipid in the females. Veith et al. (1979) reported sizable differences in bioconcentration factors of warm water and cold water fish exposed to similar concentration of PCBs, hexachlorobenzene and 1,2,4-trichlorobenzene at various temperatures. Warm water species showed a large temperature dependence on uptake up to approximately 15°C, whereas trout were less affected by temperature variation.

Other investigators point out that there is substantial evidence that effects of species, size, age, temperature and chemical concentrations can be accounted for, or are insignificant, or negligible, relative to bioconcentration (Dickson et al. 1981). Veith et al. (1979) also contend that the age and source of test fish as well as the presence of multiple pollutants in water have little effect on bioconcentration.

The bioconcentration of organic compounds by fish has been shown to be directly related to the octanol-water partition coefficient (Neely et al. 1974, Veith et al. 1979) and inversely correlated with water solubility (Metcalf 1977, Lu and Metcalf 1975, and Kapoor et al. 1973) for a variety of compounds. The basic concept is based on the tendency of lipid soluble organic chemicals to partition out of the water to compartments containing non-polar cellular components (e.g., lipids in fatty tissues of living organisms) and cell membranes. The partition of chemicals between lipids and water determines the entry of lipid soluble substances, either directly from water through cuticle, or from water to blood via the gills and from blood to tissue (Metcalf 1977). Metcalf (1977) suggests that the octanol/water partition coefficient for any organic compound can be used as a first approximation of its relative tendency to bioconcentrate in living organisms. However, he further states that the end result is clearly a function of the stability of the compound in water and the rate at which more highly partitioned degradation products are formed in the organisms (Metcalf 1977).

Norstrom, et al. (1976) developed a pollutant accumulation model to predict the concentration of PCBs and methyl mercury in tissues of yellow perch from the Ottawa River, Canada. The model relates the uptake of pollutants from food--for a given fish species--to both the energy requirements (growth and maintenance) of that species and the concentration of pollutants in its food source. The assimilation efficiency of pollutants from specific food sources is also incorporated as an element in the model. Pollutant uptake from water is based on the flow of water past the gills, the concentration of the pollutant in the water and the efficiency of removal by the gills. The metabolic rate expression in the model includes a term for estimating the effects of seasonal and annual growth in each age class. Also given is a pollutant clearance function related to body weight, but independent of metabolic rate.

Neely (1979) discussed the rates of uptake and clearance of organic substances by fish and proposed a method for estimating rate constants based on the physiology of the fish and properties of the chemical. His method expands on the work of Norstrom et al. (1976) relative to the bioenergetics of chemical uptake by fish and the work of Neely et al. (1974) showing the relationship between the octanol-water partition coefficient and bioconcentration in fish.

Neely (1979) points out that the efficiency with which a fish extracts a chemical from the water flowing past its gills is a function of the efficiency with which a chemical moves across the gill membrane, the oxygen concentration in the water and the amount of oxygen required to maintain the respiration rate of the fish. The efficiency with which a chemical moves across gill membranes (efficiency transfer coefficient) increases directly with the log of the octanol water partitioning coefficients ($K_{ow}$) and the rate constant for uptake ($k_1$) of the various compounds.

## ENVIRONMENTAL FACTORS INFLUENCING BIOCONCENTRATION

Temperature and dissolved oxygen content of the water are frequently mentioned environmental factors that influence bioconcentration of organochlorine pesticides in aquatic organisms. Both water temperature and the dissolved oxygen content influence the metabolic activity of the organism. Dickson et al. (1981), however, mention that effects of environmental factors, such as temperature, on bioconcentration and uptake depuration rates have not been adequately studied.

It has been fairly well established that those compounds with a high lipid/water partition rate and low rates of degradation and elimination may continue to concentrate in organisms as long as the organisms are exposed. That is, equilibrium between water and tissue lipids may not be achieved with stable compounds, because the time required for this to occur often exceeds the longevity of the organism (Metcalf 1977 and Hamelink et al. 1977). Conversely, a state of equilibrium may be rapidly achieved with less persistent compounds such as lindane (Gakstatter and Weiss 1967, Dickson et al. 1981) or methoxychlor which is rapidly cleared by organisms (Metcalf 1977). Table 10-1 presents a list of organic priority pollutants most subject to bioconcentration, arranged by classes of compounds.

The bioconcentration potential of any given toxic organic substance in a particular stream segment depends upon, 1) the type and quantity of biota present in the stream reach; 2) the availability of the compound for biological involvement (concentration in the water, period of exposure to receptors); and 3) the chemical nature of the compound in terms of its solubility in water, its tendency to partition to lipids and its degradation characteristics both in water and within organisms.

A number of factors influence the availability of a compound for bioconcentration, including the quantity and rate of delivery of the substance to the system, the dilution effects of receiving waters (considering volume of flow and vertical and horizontal mixing characteristics of the stream); and the nature and quantity of suspended and bedload sediment in the stream reach (including rates of transport and depostion of sediments and sorbed pollutants within the stream segment).

TABLE 10-1. ORGANIC PRIORITY POLLUTANTS MOST SUBJECT TO BIOLOGICAL UPTAKE

**Pesticides**

Aldrin
Chlordane
DDD
DDE
DDT
Dieldrin
Endrin and Endrin Aldehyde
Heptachlor Epoxide
TCDD
Polychlorinated Biphenyls

**Nitrosamines**

1,2-Diphenylhydrazine
Acrylonitrile

**Monocyclic Aromatics**

1,3-Dichlorobenzene (m-Dichlorobenzene)
1,4-Dichlorobenzene (p-Dichlorobenzene)
1,2,4-Trichlorobenzene
Hexachlorobenzene

**Phthalate Esters**

Dimethyl phthalate
Diethyl phthalate
Di-n-butyl phthalate
Di-n-octyl phthalate
Bis (2-ethylhexyl) phthalate
Butyl benzyl phthalate

Source: Callahan et al. 1979.

Obviously, a number of compound specific processes such as tendencies to undergo sorption, volatilization, photolysis, oxidation, ionization, hydrolysis and/or microbial transformation are key factors governing the availability of a compound for biological uptake within a given system. These processes, and the environmental factors that influence the nature and rates of each, are of secondary importance in discussions of bioconcentration per se, and are addressed in other portions of this report under discussions of specific processes. For example, physical transport of a substance through a system is dependent not only upon the residence time of a volume of water in the stream segment, but the form of the substance (dissolved, colloidal, sorbed onto sediments), nature of the flow, and sediment transport, deposition, resuspension, etc.

## APPLICATION OF BIOLOGICAL DATA TO FATE AND TRANSPORT MODELS

Many fate and transport models that attempt to predict the ultimate disposition of chemicals introduced to waterways incorporate only general provisions for biological uptake, storage, transformation and transport of substances in streams. For example, input data for particular models may require gross estimates of total biomass within a particular stream segment or compartment, with no consideration of the percentage contribution of various community components to the total biomass (e.g., EXAMS). Other models (e.g., PEST) accept biomass input data separated by major categories of communities based on distribution, ecological niches or behavior patterns; e.g., stationary (zoo benthos, rooted macrophytes) vs. mobile or drifting forms (fish, phytoplankton, zooplankton, and floating macrophytes). Some models emphasize bioaccumulation, but ignore chemical process (Thomann 1978). Models such as PEST incorporate provisions to accept site specific and organism specific input data reflecting current knowledge of the differential response of communities--and components within communities--to exposure, in terms of their "efficiency" as compositors, their ability to degrade or transform substances, and their potential for exporting substances across compartment or ecosystem boundaries (e.g., sediment to water, one stream segment to another, riffles to pools, streams to lakes, etc.). These features represent significant advances in model sophistication for purposes of examining the behavior of toxic substances in the context of an entire aquatic ecosystem. As experience is gained in the use of these models and as refinements are made, capabilities to predict fate and transport of toxic organic substances in natural aquatic systems can only be improved.

In using models such as EXAMS, which are designed for use as quick screening tools, only gross estimates of the quantities of particular substances that will partition to the biota in a given stream segment under steady-state conditions can be derived as output data. Even if octanol-water partition coefficients for a particular introduced chemical are known, the generated output data cannot accurately predict the quantities of a substance stored, removed or transferred by the biota unless the total biota of the stream segment consist of a known biomass for which uptake potential has been established. This is because the lipid content and the bioconcentration potential of the biota vary between community types, e.g., vascular plants, periphyton, predaceous fish, insects, mollusks, crustaceans, etc. Also, the life cycles, habits and distribution patterns of these receptors are sufficiently different that duration of exposure varies considerably.

It must be assumed that model sensitivity will continue to be improved for acceptance of input data reflecting selectivity of the various biological components as compositors of toxic organic contaminants. Information is available in the literature on uptake potential of a number of community types for selected contaminants (primarily pesticides). However, continued biological testing of other priority pollutants is essential if the role of the biota in the fate and transport of contaminants is to be adequately defined.

Table 10-2 presents a list of those biological and environmental factors that influence biological uptake of toxic organic substances in aquatic systems. Proper sampling of the biological components listed in conjunction with measurements of the key environmental factors (dissolved oxygen and water temperatures) will provide sufficient information for most types of aquatic fate and transport models that include biological uptake as a fate process. This table should not be taken as an exhaustive list of input variables for any and all aquatic fate and transport models for toxic organic substances, but rather as a minimum list of environmental parameters and community components to be measured or sampled in the field for model validation purposes.

In designing a field sampling program, the investigator must be well aware of the manner in which the data will be utilized in the model and tailor his sampling program accordingly. For example, if total biomass per compartment is identified as an input variable, the investigator must determine the dimensions of the compartment in question through appropriate field measurements and calculations and plan his sampling to adequately describe the standing crop within the compartment boundaries. He should also be well aware of any special measurement, preparation, or sample handling requirements for particular samples.

TABLE 10-2. PRINCIPAL ENVIRONMENTAL FACTORS AND BIOLOGICAL COMPONENTS THAT INFLUENCE BIOCONCENTRATION OF ORGANIC COMPOUNDS IN AQUATIC SYSTEMS

Factor

- Dissolved oxygen content
- Water temperature
- Fish
    - Total biomass per compartment
    - Size and age classes
    - Species distribution
    - Food Habits - percentage herbivores, predators
    - Resident and migratory species
- Macroinvertebrates
    - Total biomass per compartment
    - Percentages by functional groups (e.g., scrapers, shredders, collectors, etc.)
- Periphyton
    - Total biomass per compartment
    - Total diatom biomass
    - Total nondiatom biomass
- Aquatic Vascular Plants (Rooted, Floating)
    - Total biomass per compartment
- Phytoplankton
    - Total biomass per compartment
    - Total diatom biomass
    - Total nondiatom biomass
- Zooplankton and Invertebrate Drift
    - Total biomass per compartment
- Particulate organic matter (Seston)
    - Total mass per compartment

## METHODS

Problems of assessing biological influence on transport and fate of toxic organic substances in flowing systems are compounded by sampling problems associated with obtaining reliable quantitative biomass estimates of the various communities. This portion discusses stream communities and identifies key references to field sampling and measurement methods for gathering biological data that may be required for model validation purposes. Because each aquatic community or taxonomic group presents special sampling problems and requires the use of special equipment and methods, the various ecosystem components are addressed separately. Field procedures for measuring water temperature and dissolved oxygen content were described in the Biotransformation section of the report. The reader is referred to that discussion for measurement of those parameters.

## BENTHIC MACROINVERTEBRATES

### Stream Habitats and Standing Crop Estimates

Stream biologists commonly recognize three major types of stream habitats: riffles, runs, and pools. Each habitat has its own benthic community characterized by particular species associations. Biomass also normally differs greatly among the three habitats. To obtain reliable biomass estimates within a given stream reach, the proportion of each habitat must be estimated through mapping, and the biomass of each habitat estimated through appropriate sampling methods.

Because each habitat represents a discrete compartment, characterization of the communities requires use of sampling procedures and equipment tailored to the particular environment. Detailed descriptions of samplers and their operation are provided by Usinger (1956); Weber (1973); Merrit and Cummins (1978); Southwood (1978); and Resh (1979). The samplers described are known as absolute (or "quantitative") samplers because they are designed to estimate density (or biomass) per unit area of habitat (Southwood 1978). Although these are many "Quantitative" sampling methods available for deternming Biomass, the investigator should be aware that sampling devices do not always provide an absolute measure of biomass. For example it has been shown that different benthic sampling devices that collect from the same area of stream bottom provide different estimates of benthic biomass (Kroeger 1972, Pollard and Kinney 1979). This should be taken into consideration when deciding which sampling device to use to obtain biomass estimates for model input. Appendix B-1 describes the various habitats and discusses sampling procedures and field processing techniques appropriate for each.

## ALGAE

### Biomass Estimates

Biomass measurements provide important information on algal abundance and growth. Algal biomass is the amount of algal material present, i.e., the standing crop of these primary producers. Many models, predicting the consequences of nutrients, turbidity, toxicants, hydrological modifications, etc., require accurate measurements of algal biomass. Algal biomass may occur as phytoplankton--the algae suspended within the water column--or periphyton--attached algae and other algae associated with them. In lakes, especially those with poorly developed shorelines, the plankton are usually the most important primary producers. In contrast, lotic systems seldom allow for plankton development and periphyton may virtually be the only primary producers in this ecosystem, therefore occupying a very important role (Grzenda and Brehmer 1960).

Detailed discussions of the materials and methods for collection, preservation, and analysis of algal samples are found in APHA (1980), Lund and Talling (1957), Sladeckova (1962), Sournia (1978), Vollenweider (1969), Weitzel (1979), and Weber (1973). Appendix B-2 provides a discussion of methods appropriate for sampling and processing algal communities.

## FISH

### Significance as Concentrators of TOS

Fish may represent the aquatic community of principal interest in any investigation designed to assess or predict the impact of introduced contaminants on aquatic ecosystems. This is particularly true in investigations involving biocumulative toxic substances owing to the position of fish at the upper levels of the aquatic food web and the direct link they provide in the transfer of toxic biocumulative substance from the aquatic environment to man. Because fish function as compositors of toxic substances, tissue levels frequently exceed concentrations of ambient waters and of the lower trophic level food organisms by several orders of magnitude. In some cases, under conditions approaching steady-state, equilibrium may be reached between concentrations in tissue and in the surrounding water for short lived compounds.

### Sampling and Inventory Methods

Appendix B-3 examines fish sampling and inventory approaches and methods for estimating populations in a range of situations likely to be encountered in stream surveys. The advantages, disadvantages, limitations and uses of each of the various techniques and sampling devices are addressed.

Fish collection methods are frequently discussed under two categories: active and passive. Active collection methods include the use of electroshockers, seines, trawls, poisons, and angling gear. Passive methods involve the use of gill, Fyke, trammel, hoop and pound nets, and D-traps, and purchasing fish from fisherman. Other inventory methods, which normally do not involve collecting specimens, include visual observations and the use of remote sensing devices.

In some instances techniques involving diversion of entire streams have been used to make population estimates. This technique was used by Embody (1929) who diverted a trout stream and counted the fish remaining in the old channel. Needham et al. (1945) periodically made population estimates in a trout stream by diverting the water and pumping the remaining pools. Such techniques are not generally useful except in very small streams and under unusual circumstances, and will not be further discussed.

Detailed description of the various fish sampling and inventory approaches, methods, and equipment are available in the literature. Three especially useful sources are: Bagenal (1978), Weber (1973), and U.S. EPA (1979). These manuals should be studied and maintained in the possession of anyone contemplating undertaking fish surveys for any purpose.

The intent of this section is to summarize the important factors of the various approaches and techniques to enable the investigator to select the method most suited to his purpose and to the particular conditions of the stream under investigation. A combination of methods may be required to obtain the necessary information. However, the investigator will have to make that determination on a case-by-case basis.

## MACROPHYTES

### Significance as Concentrators of TOS

Macrophytes include all aquatic plants possessing a multicellular structure with cells differentiated into specialized tissue (Weber 1973). They include the mosses, liverworts, and flowering plants and range in size from nearly microscopic water meal to massive cypress trees. The most common and conspicuous stream macrophytes in most systems are the rooted vascular plants.

Macrophyte abundance may vary dramatically from one watershed to the next or even within a particular stream. Physical factors such as depth, current speed, turbidity, water level stability, and the volume of the substrate are primary factors governing the areal extent of coverage and abundance of macrophytes in most flowing waters. Obviously chemical and biological factors are also important, as nutrient deficiencies, herbicide contamination or excessive grazing by herbivores tend to reduce or eliminate macrophytes in habitats with physical characteristics suitable for abundant growths.

Macrophytes may constitute the bulk or at least a substantial portion of the total biomass in particular stream segments or habitats. Consequently, vascular plants may represent the major aquatic community component influencing fate and transport of introduced toxic organic compounds. Macrophytes are generally not considered to be as efficient concentrators of toxic organic substances as are secondary consumers, for example, but, by virtue of their sheer mass alone, the quantities of substances temporarily removed from the water column could be considerable. Although some transformation and degradation of organic compounds occur as a result of uptake by macrophytes, they undoubtedly function primarily as temporary sinks. Because macrophytes exhibit pronounced cyclic, seasonally-dependent growth patterns, the significance of their involvement in removal, transformation and transport of aquatic toxic organic substances varies considerably throughout the year. Secondly, differential rates of uptake occur among communities and species owing to physiological and metabolic differences as well as to distribution patterns and growth habits that influence duration of exposure.

### Survey Methods and Procedures

Quantitative sampling of aquatic macrophytes for purposes of obtaining absolute standing crop or biomass estimates are rarely undertaken in stream surveys. For the purposes of most surveys, estimations of the areal extent and relative abundance (e.g., dense, moderate, sparse) of the most conspicuous plant communities based on visual inspection are adequate. If several species are present, percentages of the individual taxa are often estimated and qualitative samples collected for identification purposes.

Qualitative and quantitative aquatic macrophyte sampling techniques are discussed in Slack et al. (1973), Weber (1973), and Vollenweider (1969). (Also see Appendix B-4.)

## ZOOPLANTON AND DRIFT FAUNA

### Occurrence in Flowing Systems

The invertebrate fauna in the water column of flowing systems consists both of true zooplankters and benthic forms dislodged from their normal habitats. Much of the zooplankton community of streams represents contributions from slack water areas. Hynes (1970) points out that there are no planktonic animals that are known to be restricted to flowing systems. True reproducing zooplankton occur in large, sluggish rivers, but such communities are generally very unstable. Rich zooplankton communities frequently are found downstream from reservoirs as a result of reservoir export. Such export drastically affects the trophic relationships in these reaches, with the gross effect being a great increase in total invertebrate biomass.

Drift of bottom dwelling organisms is a normal occurrence in all streams, and represents a mechanism of redistribution of populations and recolonization of denuded areas. The total biomass in drift during periods of peak movement frequently exceeds the total standing crop of the established benthos. Drift organisms are important forage items for stream fish and periods of peak feeding activity frequently coincide with periods of maximum benthic drift.

Stream biological surveys designed to investigate invertebrate density and distribution for purposes of determining fish food availability, water quality relationships or similar purposes should include measurements of drift fauna as one component of the stream benthos. The drift community represents components of benthic organisms associated directly with the stream bottom as well as those animals associated with littoral vegetation that through behavioral or catastrophic (e.g., flooding) activity have dislodged from the substrate. Drift represents a mechanism of transport of considerable invertebrate biomass. Much of the community associated with behavioral drift will become reestablished in downstream reaches--although predation takes a heavy toll--representing a mechanism of redistribution of organisms and associated bioconcentrated substances. Organisms dislodged from their habitats as a result of heavy flooding or disturbances to the stream bed or littoral vegetation are frequently badly mutilated and are unable to recolonize downstream reaches. Some of these animals are eaten by fish while others are deposited along with debris in slack water areas including lakes and reservoirs with habitats unsuitable for colonization.

Procedures for sampling stream drift organisms are described in Weber (1973), Elliott (1970), Waters (1962, 1969) and others. Appendix B-5 provides a discussion of field methods appropriate for obtaining drift biomass estimates.

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# PHYSICAL TRANSPORT

## TRANSPORT

Toxic organic chemicals, at low concentrations in natural waters, exist in a dissolved phase and a sorbed phase. Dissolved substances are transported by water movement with little or no "slip" relative to the water. They are entirely entrained in the current and move at the water velocity. Likewise, organics which are sorbed to colloidal material or fine suspended solids are essentially entrained in the current, but they may undergo additional transport processes such as sedimentation and deposition or scour and resuspension. These processes may serve to retard the movement of the sorbed substances relative to the water movement. Thus in order to determine the fate and transport of toxic organic substances, we must know both the water movement and sediment movement.

### Water Budget

The importance of a good water budget should not be ignored. Physical transport of water in a clearly defined ecosystem is accounted for in a water balance.

$$\text{Accumulation of } H_2O = \text{Inflows} + \overset{\text{Direct}}{\text{Precipitation}} - \text{Outflows} - \text{Evaporation}$$

$$(+\ \text{Infiltration} - \text{Exfiltration} + \text{Overland Runoff})$$

Water can be stored within lakes or rivers by a change in elevation or stage. Inflows and outflows should be gaged or measured over the period of investigation. Precipitation gages and evaporation pans can be utilized with sufficient accuracy. In the best of situations, it is possible to achieve an annual water balance within five percent (total inflows are within 5 percent of total outflows). Confounding factors include infiltration, exfiltration, and overland runoff.

### Transport of Chemicals in Water

The transport of toxic chemicals in water principally depends on two phenomena: advection and dispersion. Advection refers to movement of dissolved or fine particulate material at the current velocity in any of three directions (longitudinal, lateral or transverse, and vertical). Dispersion refers to the process by which these substances are mixed within the water column. Dispersion can also occur in three directions. There are a number of processes which contribute to the mixing (dispersion) process:

1. Molecular diffusion. This is the mixing of dissolved chemicals due to the random walk of molecules within the fluid. It is caused by kinetic energies of molecular vibrational, rotational, and translational motion. In essence, molecular diffusion corresponds to an increase in entropy whereby dissolved substances move from regions of high concentration to regions of low concentration according to Fick's laws of diffusion. It is an exceedingly slow phenomena, such that it would take on the order of 10 days for 1 mg/l of dissolved substance to diffuse through a 10 cm water column from a concentration of 10 mg/l. It is generally not an important process in the transport of dissolved substances in natural waters except relating to transport through thin and stagnant films at the air-water interface or transport through sediment pore water.

2. Turbulent Diffusion. Turbulent or eddy diffusion refers to mixing of dissolved and fine particulate substances due to micro-scale turbulence. It is an advective process at the microscale level caused by eddy fluctuations in current velocity. Shear forces within the body of water are sufficient to cause this form of mixing. It is several orders of magnitude larger than molecular diffusion and is a contributing factor to dispersion. Turbulent diffusion can occur in all three directions, but is often anisotrophic (i.e., there exist preferential directions for turbulent mixing due to the direction and magnitude of shear stresses).

3. Dispersion. The interaction of turbulent diffusion with velocity profiles in the water body causes a still greater degree of mixing known as dispersion. Transport of toxic substances in streams and rivers is predominantly by advection, but transport in lakes and estuaries is often dispersion controlled. Velocity gradients are caused by shear forces at the boundaries of the water body, such as, vertical profiles due to wind shear at the air-water interface, and vertical and lateral profiles due to shear stresses at the sediment-water and bank-water interfaces. Also velocity gradients can develop within the water body due to channel morphology, the sinuousity and meandering of streams, and thermal or density stratification and instabilities in lakes and estuaries. Morphological causes of dispersive mixing in rivers include dead spots, side channels, and pools where back-mixing occurs. When turbulent diffusion causes a parcel of fluid containing dissolved substances to change position, that parcel of fluid becomes entrained in the water body at a new velocity, either faster or slower. This causes the parcel of fluid and the toxic substance to mix forward or backward relative to its neighbors. The mixing process is called dispersion and results in a mass flux of toxic substances from areas of high concentration to areas of low concentration, analagous to molecular diffusion, but at a much more rapid rate. The mass flux rate can be described by Fick's first law of diffusion:

$$J = - K A \frac{dc}{dx} \qquad (1)$$

$J$ = max flux rate, M/T
$K$ = diffusion or dispersion coefficient, $L^2/T$
$A$ = cross sectional area through which diffusion occurs, $L^2$
$\frac{dc}{dx}$ = concentration gradient, $M/L^3\text{-}L$

## Advective-Dispersive Equation

The basic equation describing advection and dispersion of dissolved matter is based on the principle of conservation of mass and Fick's law. For a conservative substance, the principle of conservation of mass can be stated:

$$\begin{bmatrix}\text{Rate of change}\\ \text{of mass in}\\ \text{control volume}\end{bmatrix} = \begin{bmatrix}\text{Rate of change of}\\ \text{mass in control}\\ \text{volume due to}\\ \text{advection}\end{bmatrix} + \begin{bmatrix}\text{Rate of change of}\\ \text{mass in control}\\ \text{volume due to}\\ \text{diffusion}\end{bmatrix} - \begin{bmatrix}\text{Transformation}\\ \text{Reaction Rates}\\ \text{(Degradation)}\end{bmatrix}$$

$$\frac{\partial C}{\partial t} = -u_i \frac{\partial C}{\partial x_i} + \frac{\partial}{\partial x_i}\left(\varepsilon_i \frac{\partial C}{\partial x_i}\right) - R \qquad (2)$$

where $C$ = concentration, $M/L^3$
$t$ = time, T
$u_i$ = average velocity in the i'th direction, L/T
$x_i$ = distance in the i'th direction, L
$R$ = reaction transformation rate, $M/L^3\text{-}T$

$\varepsilon_i$ is the diffusion coefficient in the i'th direction. For laminar flow, $\varepsilon_i = \varepsilon_M$, the coefficient of molecular diffusion. For turbulent flow, $\varepsilon_i = \varepsilon_T + \varepsilon_M$, where $\varepsilon_T$ is the coefficient of turbulent diffusion. In Fickian diffusion theory, it is assumed that dispersion resulting from turbulent open-channel flow is exactly analogous to molecular diffusion. The dispersion coefficients in the x, y, and z directions are assumed to be constants, given by $K_x$, $K_y$ and $K_z$. The resulting equation, expressed in Cartesian coordinates is:

$$\frac{\partial C}{\partial t} + u_x \frac{\partial C}{\partial x} + u_y \frac{\partial C}{\partial y} + u_z \frac{\partial C}{\partial z} = K_x \frac{\partial^2 C}{\partial x^2} + K_y \frac{\partial^2 C}{\partial y^2} + K_z \frac{\partial^2 C}{\partial z^2} - R \qquad (3)$$

the solution of equation (3) depends on the values of $K_x$, $K_y$ and $K_z$. Various authors have arrived at equations to approximate the values of the dispersion coefficients (K) in the longitudinal (x), lateral (y), and vertical (z) directions.

## Longitudinal Dispersion Coefficient in Rivers

Liu (1977) used the work of Fischer (1967) to develop an expression for the longitudinal dispersion coefficient in rivers and streams ($K_x$, which has units of length squared per time):

$$K_x = \beta \frac{u_x^2 B^3}{U_\star A} = \beta \frac{O_B^2}{U_\star D^3} \tag{4}$$

where Liu (1978) defined,

$\beta = 0.5 \left(\frac{U_\star}{u_x}\right)^2$

$D$ = mean depth, L

$B$ = mean width, L

$U_\star$ = bed shear velocity, L/T

$u_x$ = mean stream velocity, L/T

$A$ = cross sectional area, $L^2$

$O_B$ = river discharge, $L^3/T$

$\beta$ does not depend on stream morphometry but on the dimensionless bottom roughness. Based on existing data for $K_x$ in streams, the value of $K_x$ can be predicted to within a factor of six by equation (4). The bed shear velocity is related empirically to the bed friction factor and mean stream velocity:

$$U_\star = \sqrt{\frac{To}{\rho}} = \sqrt{\frac{f}{8} u_x^2} \tag{5}$$

in which To = bed shear stress, $M/L\text{-}T^2$
f = friction factor ≈0.02 for natural, fully turbulent flow
$\rho$ = density of water, $M/L^3$

## Lateral Dispersion Coefficient in Rivers

Elder (1959) proposed the equation for predicting the lateral dispersion coefficient, $K_y$:

$$K_y = \phi D U_\star \tag{6}$$

where $\phi$ is equal to 0.23. The value of $\phi = 0.23$ was obtained by experiments in long, wide laboratory flumes.

Many authors have since investigated the value of $\phi$ in both laboratory flumes and natural streams. Sayre and Chang (1968) reported $\phi = 0.17$ in a straight laboratory flume. Yotsukura and Cobb (1972) report values of $\phi$ for natural streams and irrigation canals varying from 0.22 to 0.65, with most values being near 0.3. Other reported values of $\phi$ range from 0.17 to 0.72. The higher values for $\phi$ are all for very fast rivers. The conclusions drawn are that; 1) the form of equation (6) is correct predicting $K_y$, but $\phi$ may vary, and 2) application of Fickian theory to lateral dispersion is correct as long as there are no appreciable lateral currents in the stream.

Okoye (1970) refined the determination of $\phi$ somewhat by use of the aspect ratio, $\lambda = D/B$, the ratio of the stream depth to stream width. It was found that $\phi$ decreased from 0.24 to 0.093 as $\lambda$ increased from 0.015 to 0.200.

The effect of bends in the channel of $K_y$ is significant. Yotsukura and Sayre (1976) reported that $\phi$ varies from 0.1 to 0.2 for straight channels, ranging in size from laboratory flumes to medium size irrigation channels; $\phi$ varies from 0.6 to 10 in the Missouri River, and $\phi$ varies from 0.5 to 2.5 in curved laboratory flumes. Fischer (1968) reports that higher values of $\phi$ are also found near the banks of rivers.

## Vertical Dispersion Coefficient in Rivers

Very little experimental work has been done on the vertical dispersion coefficient, $K_z$. Jobson and Sayre (1970) reported a value for marked fluid particles of:

$$K_z = \kappa U_* z \left(1 - \frac{z}{D}\right) \tag{7}$$

for a logarithmic vertical velocity distribution. $\kappa$ is the von Karman coefficient, which is shown, experimentally, to be approximately = 0.4 (Tennekes and Lumley, 1972). Equation (7) agrees with experimental data fairly closely.

## Vertical Eddy Diffusivity in Lakes

Vertical mixing in lakes is not mechanistically the same as that in rivers. The term "eddy diffusivity" is often used to describe the turbulent diffusion coefficient for dissolved substances in lakes. Chemical and thermal stratification serve to limit vertical mixing in lakes, and the eddy diffusivity is usually observed to be a minimum at the thermocline.

Many authors have correlated the vertical eddy diffusivity in stratified lakes to mean depth, hypolimnion depth, and to the stability frequency. Mortimer (1941) first correlated the vertical diffusion coefficient with the mean depth of the lake. He found the following relationship:

$$K_z = 0.0142\ Z^{1.49} \tag{8}$$

in which $K_z$ = vertical eddy diffusivity, $m^2$/day
$Z$ = mean depth, m

Vertical eddy diffusivities can be calculated from temperature data by solving the vertical heat balance or by the simplified estimations of Edinger and Geyer (1965). Schnoor and Fruh (1979) have demonstrated that the mineralization and release of dissolved substances from anaerobic sediment can be used to calculate average hypolimnetic eddy diffusivities. This approach avoids the problem of assuming that heat (temperature) and mass (dissolved substances) will mix with the same rate constant, i.e., that the eddy diffusivity must equal the eddy conductivity. A summmary of dispersion coefficients and their order of magnitude appears below.

| | Dispersion Coefficient, $cm^2/sec$ |
|---|---|
| Molecular Diffusion | $10^{-5}$ |
| Compacted Sediment | $10^{-7} - 10^{-5}$ |
| Bioturbated Sediment | $10^{-5} - 10^{-4}$ |
| Lakes - Vertically | $10^{-2} - 10^{1}$ |
| Large Rivers - Lateral | $10^{-2} - 10^{3}$ |
| Large River - Longitudinal | $10^{4} - 10^{5.5}$ |
| Estuaries - Longitudinal | $10^{6} - 10^{7}$ |

## Choosing a Transport Model

It is possible to estimate the relative importance of advection compared to dispersion with the Peclet number:

$$Pe = uL/K \qquad (9)$$

in which $Pe$ = Peclet number, dimensionless
$u$ = mean velocity, $L/T$
$L$ = segment length, $L$
$K$ = dispersion coefficient, $L^2/T$

If the Peclet number is significantly greater than 1.0, advection predominates; if it is much less than 1.0, dispersion predominates the transport of dissolved, conservative substances.

If there is a significant transformation rate, the reaction number can be helpful:

$$\text{Rxn No.} = \frac{kK}{u^2} \qquad (10)$$

where $k$ = the first order reaction rate constant, $T^{-1}$. If the reaction number is less than 0.1, then advection predominates and a model approaching plug flow is appropriate. If the reaction number is greater than 10, then dispersion controls the transport and the system is essentially completely mixed. Otherwise a number of compartments in series will best simulate the prototype water body.

## Compartmentalization

Compartmentalization refers to the segmentation of model ecosystems into various "completely-mixed" boxes of known volume and interchange. Interchange between compartments is simulated via bulk dispersion or equal counterflows between compartments. Compartmentalization is a popular assumption in fate and transport modeling because the completely-mixed assumption reduces the set of partial differential equation (in time and space) to one of ordinary differential equations (in time only). Nevertheless it is possible to recover some coarse spatial information by introducing a number of interconnected compartments.

A completely-mixed flow-through (CMF) compartment contains an ideal mixing of fluid in which turbulence is so large that no concentration gradients can exist within the compartment. This corresponds to the assumption that $K_{x,y,z} = \infty$. Equation (3) reduces to:

$$\begin{bmatrix}\text{Accumulation of Mass}\\ \text{w/in Compartment j}\end{bmatrix} = \begin{bmatrix}\text{Mass}\\ \text{Inflows}\\ \text{to j}\end{bmatrix} + \begin{bmatrix}\text{Dispersive}\\ \text{Inflows}\\ \text{to j}\end{bmatrix} - \begin{bmatrix}\text{Mass}\\ \text{Outflows}\\ \text{from j}\end{bmatrix} - \begin{bmatrix}\text{Dispersive}\\ \text{Outflows}\\ \text{from j}\end{bmatrix} - \begin{bmatrix}\text{Transformation}\\ \text{Reactions}\\ \text{w/in j}\end{bmatrix}$$

$$V_j \frac{dC_j}{dt} = \sum_{k=1}^{n} Q_{j,k}C_k + \sum_{k=1}^{n} Q'_{j,k}C_k - \sum_{k=1}^{n} Q_{k,j}C_j - \sum_{k=1}^{n} Q'_{k,j}C_j - kC_jV_j \qquad (11)$$

in which $V_j$ = volume of j compartment, $L^3$

$C_j$ = concentration within j compartment, $M/L^3$

$t$ = time, T

$n$ = number of adjacent compartments to j

$Q_{j,k}$ = inflow from compartment k to compartment j, $L^3/T$

$C_k$ = concentration in compartment k, $M/L^3$

$Q'_{j,k}$ = dispersive (interchange) flow from k to j, $L^3/T$

$Q_{k,j}$ = outflow from j to k, $L^3/T$

$Q'_{k,j}$ = dispersive (interchange) flow from j to k, $L^3/T$

$k$ = pseudo-first order rate constant for transformation, $T^{-1}$

and $Q'_{j,k} = Q'_{k,j}$ for a symmetric matrix with zero diagonal

Equation (11) can be rewritten in terms of bulk dispersion coefficients:

$$V_j \frac{dC_j}{dt} = \sum_{k=1}^{n} Q_{j,,}C_k - \sum_{k=1}^{n} Q_{k,j}C_j + \sum_{k=1}^{n} K'_{j,k}A_{j,k}(C_k - C_j)/\ell_{j,k} - kC_jV_j \qquad (12)$$

where $K'$ = bulk dispersion coefficient, $L^2/T$

$A_{j,k}$ = interfacial area between compartments j and k, $L^2$

$\ell_{jk}$ = distance between midpoints of compartments, L

There is one mass balance equation (e.g. equation 12) for each of n compartments. This set of ordinary differential equations is solved simultaneously by numerical computer methods.

Bulk dispersion coefficients between compartments are dependent on the scale chosen for the compartments. They are not equivalent to measured dispersion coefficients from dye studies (these are usually derived from the continuous partial differential equations). The very nature of the compartmentalized system introduces considerable mixing into the model. Such mixing or numerical dispersion is in addition to the bulk dispersion specified by the bulk dispersion coefficient.

Streams and swift-flowing rivers may approach a 1-D plug flow system (i.e. the water is completely mixed in the lateral and vertical dimensions, but there is no mixing in the longitudinal dimension). In an ideal plug flow system, the longitudinal dispersion coefficient is equal to zero since there is no forward or backward mixing. For this case an infinite number of compartments (of infinitestimal length in in the longitudinal direction) would be required in order to produce zero longitudinal mixing. Since it is impossible to specify an infinite number of compartments, one chooses a finite number of compartments and accepts the artificial dispersion which accompanies that choice. One method of estimating the artificial or numerical dispersion of a compartmentalized model for an ideal, plug flow system is given by equation (13).

$$E_x = \frac{u\Delta x}{2}\left(1 - \frac{u\Delta t}{\Delta x}\right) \qquad (13)$$

where $E_x$ = artificial numerical dispersion coefficient, $L^2/T$
$u$ = mean longitudinal velocity, L/T
$\Delta x$ = longitudinal length of equal spaced compartments, L
$\Delta t$ = time step for numerical computation, T

One approach would be to set the artificial dispersion coefficient equal to the measured or estimated dispersion coefficient from equation (4). With this approach it is not necessary to use bulk dispersion coefficients; rather, one allows the artificial dispersion of the model to account for the actual dispersion of the prototype.

In general most river simulations require many compartments due to their nearly plug flow nature, as indicated by their large Peclet number (equation 9). The greater the number of compartments, the greater the tendency towards plug flow conditions. It is a poor choice to simulate a riverine environment with one completely-mixed compartment.

Lakes, reservoirs, and embayments may require a number of compartments if one desires some spatial detail, such as concentration profiles. These compartments should be chosen to relate to the physical and chemical realities of the prototype. For example, a logical choice for a deep lake is to have two compartments: an epiliminion and hypolimnion. Mixing between compartments can be accomplished by interchanging flows:

$$J = Q_{ex}D_{epi} - Q_{ex}C_{hypo} \tag{14}$$

where $J$ = net mass flux from epilimnion to hypolimnion due to vertical mixing, M/T

$Q_{ex}$ = exchange flow, $L^3/T$

$C$ = concentration of chemical, $M/L^3$

The magnitude of the interchange flow, $Q_{ex}$, can be determined from tracer studies or from temperature profiles and simulations. Bulk dispersion coefficients can then be calculated based on the interchange flow as $Q_{ex}\ell_{epi\ hypo}/A$.

Sometimes only coarse information is required for a given use of the model. There are many lucid examples in the literature of modeling efforts based on very simple transport models. The U.S. Great Lakes have often been simulated as single compartment, completely-mixed lakes in series (Chapra, 1977). Toxic chemical screening methodologies are usually based on organic chemical properties that are known only within an order-of-magnitude. In such cases it may not be necessary to simulate transport with great accuracy. There exists a distinct trade-off between errors in transport formulations and errors in reaction rate constants as shown in Table 11-1. If the sum of the pseudo-first order reaction rate constant is accurately determined in the field or laboratory, then an accurate model simulation will require a realistic transport formulation.

For example, consider a hypothetical lake whose steady state outlet concentration of a toxic chemical is determined to be 0.01 times the inflow concentration. Suppose the hydraulic detection time, $\tau$, of the lake is 10 days, and the transformation reaction rate constant is determined to be 1.0/day ($k\tau=10$). The lake is behaving like three compartments-in-series according to Table 11-1. However the model calibration would have required a reaction rate constant of 10.0/day in order to obtain the observed result of $C/Co = 0.01$ if only the completely-mixed compartment had been assumed.

TABLE 11-1. OUTFLOW CONCENTRATION DIVIDED BY/INFLOW CONCENTRATION AT STEADY STATE AS A FUNCTION OF NUMBER OF COMPARTMENTS AND $k\tau$

| | C/Co VALUES<br>Rate Constant x Detention Time | | | | |
|---|---|---|---|---|---|
| | $k\tau=0.01$ | $k\tau=0.1$ | $k\tau=1.0$ | $k\tau=10$ | $k\tau=100$ |
| CMF* (1-compart.) | 0.99 | 0.91 | 0.50 | 0.09 | 0.01 |
| 3-compart.+ | 0.99 | 0.91 | 0.42 | 0.01 | $2 \times 10^{-5}$ |
| 10-compart.+ | 0.99 | 0.91 | 0.39 | $1 \times 10^{-3}$ | $4 \times 10^{-11}$ |
| PF† ($\infty$ compart.) | 0.99 | 0.90 | 0.37 | $5 \times 10^{-5}$ | $4 \times 10^{-44}$ |

* $C/Co = 1/(k\tau+1)$.
+ $C/Co = 1/([k\tau/n]+1)^n$
† $C/Co = \exp(-k\tau)$

where $\tau$ = total hydraulic detection time
$k$ = first order reaction rate constant
where $n$ = number of compartments

In summary, the first approach should be to choose compartments that correspond to the morphometric features of the aquatic ecosystem prototype. If better than order of magnitude accuracy is required in the model, one can estimate dispersion coefficients from semi-empirical equations, e.g. equations (4) through (8). If still greater accuracy is desired, one should utilize tracer studies and simulations. Temperature and velocity are thermal and momentum "tracers" that can be used to calibrate the mixing characteristics of the water body. Salinity can often serve as a conservative tracer in estuarine studies, but dye or radioisotope tracers generally yield the best quality information.

## SEDIMENT TRANSPORT

Chemicals can be associated with sediments by adsorption (electrostatic surface forces), chemisorption (chemical bonding between the chemical and surface), or ion exchange (surface exchange of ionic species). Suspended solids (also termed "suspended sediment") can undergo transport in the horizontal and vertical dimensions.

Bed load transport includes those particles which saltate, bounce, roll, or flow within a few particle diameters of the bottom sediment. In rivers, downstream transport of suspended sediment includes particles which settle to the bottom and very fine particles which do not settle substantially and are termed "wash load". Total sediment transport consists of suspended load plus bed load. It comprises sediments of autochthonous (internally produced by primary and secondary aquatic production) and allochthonous (externally produced from land and air) origin. Suspended and bed load sediments consist of a distribution of particle types and sizes, including those classified as sand, silt, and clay.

## Partitioning

A chemical is partitioned into a dissolved and particulate adsorbed phase based on its sediment-to-water partition coefficient, Kp (Karickhoff et al., 1979). The dimensionless ratio of the dissolved to the particulate concentration is the product of the partition coefficient and the concentration of suspended solids, assuming local equilibrium.

$$Cp/C = KpM \tag{15}$$

where $Cp$ = particulate chemical concentration, $\mu g/\ell$
$C$ = dissolved chemical concentration, $\mu g/\ell$
$Kp$ = sediment/water partition coefficient, $\ell/kg$
$M$ = suspended solids concentration, $kg/\ell$

The particulate and dissolved concentrations can be calculated from knowledge of the total concentration, $C_T$, as stated in equations (16) and (17).

$$Cp = \frac{KpM}{1 + KpM} C_T \tag{16}$$

$$C = \frac{1}{1 + KpM} C_T \tag{17}$$

These concentrations can be calculated for the water column or the bed sediment, by using the concentration of suspended solids in the water (M) or in the bed ($M_b$), respectively.

## Suspended Load

The suspended load of solids in a river or stream is defined as a flow rate times the concentration of suspended solids, e.g. kg/day or tons/day. The mean suspended load of a river is greatly weighted by peak flows. Peak flows cause large inputs of allochthonous material from errosion and runoff as well as increases in scour and resuspension of bed and bank sediment.

The average suspended load is not equal to the average flow times the average concentration, as stated in equations (18) and (19).

$$\overline{Q} \times \overline{C} \neq \overline{QC} \tag{18}$$

$$\overline{QC} = \overline{Q} \times \overline{C} + \overline{Q'C'} \tag{19}$$

The mean fluctuation of mass, $\overline{Q'C'}$, is usually greater than the first term of equation (19) and contributes greatly to the average suspended load. These equations hold true for the mass of suspended solids as well as the mass of adsorbed chemical.

## Bed Load

Several formulas have been reported to calculate the rate of sediment movement very near the bottom. These were developed for rivers and non-cohesive sediments, i.e. fine-to-coarse sands and gravel. It is important to note that it is not sands, but rather silts and clays, which transport most sorbed chemicals. Therefore these equations are of limited predictive value in environmental exposure assessments. Generally bed load transport is a small fraction of total sediment transport (suspended load plus bed load). However, in estuaries, bed load transport of fine silts and clays may be an important contribution to the fate of chemical contaminants. Unfortunately, predictive equations have not been developed for bed load transport in such applications. For a detailed discussion of available techniques the reader is referred to the methods section presented below.

## Sedimentation

Suspended sediment particles and adsorbed chemicals are transported downstream at nearly the mean current velocity. In addition, they are transported vertically downward by their mean sedimentation velocity. Generally the particles settle, according to Stoke's Law, in proportion to the square root of the particle diameter and the difference between sediment and water densities. One modification of Stoke's Law that is frequently used to calculate particle fall velocities is the Rubey equation (1933):

$$w = F_1 \sqrt{\frac{\gamma_s - \gamma}{\gamma} g d_s} \qquad (20)$$

in which

$w$ = particle fall velocity, ft/sec
$\gamma_s$ = specific weight of sediment particle, lbs/ft$^3$
$\gamma$ = specific weight of water, lbs/ft$^3$
$g$ = gravitational constant, ft/sec$^2$
$d_s$ = sediment particle diameter, ft

$$F_1 = \sqrt{\frac{2}{3} + \frac{36\ \nu^2}{g d_s{}^3(\gamma_s/\gamma - 1)}} - \sqrt{\frac{36\ \nu^2}{g d_s{}^3(\gamma_s/\gamma - 1)}} \qquad (21)$$

$\nu$ = kinematic viscosity of water, ft$^2$/sec

Generally it is the washload (fine silt and clay-size particles) which carry most of the adsorbed chemical. These materials have very small fall velocities, on the order of 0.3 m/day for clays of 2-4 μm nominal diameter and 3 m/day for silts of 10-20 μm nominal diameter.

Once a particle reaches the bed, there exists a certain probability that it can be scoured from the bed sediment and resuspended. The difference between sedimentation and resuspension represents net sedimentation. Often it is possible to utilize a net sedimentation rate constant in the fate and transport model to account for both processes. In many ecosystems where the bed is aggrading, sedimentation is much larger than resuspension, Schnoor and McAvoy (1981). The net sedimentation rate constant can be calculated as follows:

$$k_s = \frac{w}{H} - k_u \simeq \frac{w}{H} \qquad (22)$$

where $k_s$ = net sedimentation rate constant, 1/T
$w$ = mean particle fall velocity, L/T
$H$ = mean depth, L
$k_u$ = scour/resuspension rate constant, 1/T

### Scour/Resuspension

Quantitative relationships to predict scour and resuspension of cohensive sediments are difficult to develop due to the number of variables involved. Sayre and Chang (1968) reported on the vertical scour and dispersion of silt particles in flumes. DiToro et al. (1982) recommended a resuspension velocity ($W_{rs}$) of about 1-30 mm/yr based on model calibration studies. The turbulent vertical eddy diffusivity for sediment ($\varepsilon_s$) is also related to the scour coefficient and/or a resuspension velocity.

Under steady state, the sedimentation of suspended sediment must equal the scour and resuspension of sediment.

$$w\,\overline{C} + \varepsilon_s \frac{\partial \overline{C}}{\partial z} = 0 \qquad (23)$$

where $w$ = sedimentation velocity, L/T
$\varepsilon_s$ = suspended sediment vertical eddy diffusivity, $L^2/T$
$\overline{C}$ = concentration of suspended sediment, $M/L^3$

However under time-varying conditions, the boundary condition at the bed-water interface is more complex. According to Onishi and Wise (1979) the following equation applies, based on the work of Krone (1962) and Partheniades (1965).

$$(1-p)\,w\,\overline{C} + \varepsilon_s \frac{\partial \overline{C}}{\partial z} = S_D - S_R \qquad (24)$$

where $p$ = probability that descending particle will "stick"

$S_D$ = rate of bed deposition, $M/L^2$-T

$$S_D = \frac{2w\bar{C}}{h}\left(1 - \frac{\tau_o}{\tau_{cD}}\right)$$

$S_R$ = rate of bed scour, $M/L^2$-T

$$S_R = M_j\left(\frac{\tau_o}{\tau_{cR}} - 1\right)$$

$M_j$ = erodibility coefficient, $M/L^2$-T

$\tau_{cR}$ = critical bed sheaar required for resuspension, $M/L$-$T^2$

$\tau_{cD}$ = critical bed shear stress which prevents deposition, $M/L$-$T^2$

$h$ = ratio of depth of water to depth of active bed layer

Equation (24) shows that the bed can either be aggrading or degrading at any time or location depending on the relationship between $S_D$ and $S_R$.

## Desorption/Diffusion

In addition to sedimentation and scour/resuspension, an adsorbed chemical can desorb from the bed sediment. Likewise dissolved chemical can adsorb from the water to the bed. Both pathways can be presented by a diffusion coefficient ($K_b$) and a concentraation gradient or difference between water and sediment concentrations.

## SUMMARY

Sediment mass balances must include terms for advection, sedimentation, scour/resuspension, and possibly vertical or longitudinal dispersion. At the bottom, bed load movement may be included. Processes which affect the fate of dissolved substances include desorption from the bed (or adsorption from the water column), advection, dispersion, and transformation reactions. Adsorbed particulate chemical is removed from the water column by sedimentation and returned to the water column by scour. Models which are used to evaluate fate and transport should include these processes.

Often it is possible to neglect the kinetics of adsorption and desorption in favor of a local equilibrium assumption. Over the time scales of interest, this may be a good assumption. Also bed load movement is sometimes small relative to wash load movement and can be neglected. Under steady state conditions, net sedimentation rates are often used to simplify the transport of sedimentation and scour. All of these assumptions have their applications but should be carefully considered in each model application.

## METHODS

In designing a program to field validate aquatic fate and transport models for toxic organics substances, special consideration must be given to selection of a study area. The investigator must be familiar with the input requirements of the particular model in question, and select candidate study sites that minimize complexing influences. That is, the least complex study area that meets the minimal requirements for the model in question should be selected whenever possible. Consideration must be given to such factors as: stability of the flow regime; uniformity of the stream channel; sources of pollutants and inflow within the study area; flow diversions and obstructions; availability of historical data; accessibility to the stream; and relative ease in obtaining flow data and required measurements. It is particularly critical that pollution and dilution influences that are not easily quantified (e.g., non point sources, ground water inflows, intermittent inflows, discharges, etc.) are avoided whenever possible. It is also highly desirable to base parameter field inputs on measured values rather than calculated values whenever possible. For example, non point source loading is not easily measured in most situations, but a number of models are available that predict NPS loading functions and rates. The difficulties associated with incorporation of such calculated input values are obvious; they introduce a potential soure of error in input values of unknown magnitude, thereby reducing the level of confidence in derived output values.

Table 11-2 presents a partial list of site specific environmental input values currently required or anticipated as future requirements for aquatic fate and transport modes such as EXAMS, TOXICS, PEST, etc. The following addresses field methodologies most appropriate for obtaining the required field data for each parameter.

## COMPARTMENT DIMENSIONS

### Length (M)

The length of a stream segment (compartment) can be determined by two principal methods: 1) measurement from maps of suitable scale and accuracy (e.g., USGS 15 min. quadrangle maps; or US Coast Guard Navigation Charts); or 2) direct field measurements. Measurements from maps can be accomplished using map measurer devices or with a set of calibrated map dividers (Welch 1948). Field measurements can be determined through use of steel tapes or tag lines, by chaining along the bank or with the use of calibrated range finders.

### Width (M)

Stream width measurements can sometimes be determined from maps of appropriate scale and accuracy following procedures described by Welch (1948) and Wetzel and Likens (1979). More frequently, however, width measurements are made in the field from cableways or bridges, from a boat or by wading following techniques described by Buchanan and Somers (1969). Cableways and bridges can be marked with paint at measured intervals to indicate distances. Steel tapes or tag lines marked with solder beads or tags at regular intervals

TABLE 11-2. SITE SPECIFIC ENVIRONMENTAL INPUTS TO AQUATIC FATE AND TRANSPORT MODELS FOR PHYSICAL TRANSPORT

Compartment Dimensions

- Length (M)
- Width (M)
- Height (Depth) (M)
- Volume (M$^3$)
- Surface Area (M$^2$)
- Cross Section Area (M$^2$)
- Distance Between Compartment Centers (M)

Water, Sediments, Biota, and Organic Particulate Matter Entering Compartments

- Rainfall (mm/h)
- Groundwater (m$^3$/h)
- Interflow (m$^3$/h)
- Nonpoint Source Water volume (M$^3$/h)
- Tributary Water inflow (M$^3$/h)
- Streamflow (M$^3$/s)
- Nonpoint Source Sediments (kg/h)
- Tributary Sediment inflow (kg/h)
- Suspended Sediments (kg/h)
- Bedload Sediments (kg/h)
- Biota
- Particulate Organic matter

Measurements Within Compartments

- Suspended Sediments
  - Concentration determination (mg/l)
  - Discharge calculation (kg/D)
  - Size distribution (%)
  - Settling Velocity (%)
  - Organic Matter (%)

- Bedload Sediments and Bed Material
  - Discharge (kg/D)
  - Size distribution (%)
  - Organic matter (%)
  - Bulk density (c/cm$^3$)
  - Water content (%)
  - Biota

- Water Column
  - Water Temperature (C)
  - Dissolved oxygen (mg/l)
  - Dissolved organic carbon (mg/l)
  - Total organic carbon (mg/l)
  - Biota
  - Eddy diffusivity (M$^2$/hr)

(continued)

TABLE 11-2. (Continued)

Losses from Compartment
- Suspended sediments
- Bedload sediments
- Water volume
- Biota
- Particulate organic matter
- Evaporation

can be used from boats or when wading to measure distences. The important factor to keep in mind when making stream width measurements is that stream width may vary dramatically with water level and longitudinal location in the channel. In natural stream channels a number of measurements are required to determine the mean width for the segment or compartment of interest (Buchanan and Somers 1969).

### Height (Depth) (M)

The height of a given water compartment usually coincides with the depth of the stream or the designated stratum. Depth measurements are generally made along several transects within a compartment (segment) using conventional techniques described by Welch (1948), Buchanan and Somers (1969), and Betson (1978). In large streams a recording depth finder mounted on a boat simplifies depth measurements and an analog strip chart recorder provides a permanent record of depth data.

### Volume ($M^3$)

The volume of water within a compartment at any given moment can be computed from the previously described measurements (L x H x W).

### Surface Area ($M^2$)

The surface area of a compartment is determined from the product of length and width measurements previously discussed. This applies both to water and benthic compartments.

### Cross Section Area ($M^2$)

Cross sectional area is restricted to water compartment applications and represents the product of width and mean depth.

### Distance Between Compartment Centers (M)

Linear distances between compartment centers are determined from maps of appropriate scale and accuracy or measured directly in the field following techniques described for determining stream length.

## WATER, SEDIMENTS AND BIOTA ENTERING COMPARTMENTS

### Rainfall (mm/h)

A variety of methods and instruments are available for measuring rainfall and other forms of precipitation. Basically, the ordinary rain gage consists of a funnel that leads into a collector with some sort of measuring device that is operated manually or automatically. Pogerman (1980) presents detailed discussions of methodologies for rainfall (and other forms of precipitation) measurements.

### Groundwater ($M^3$/h)

Quantification of groundwater contribution to the total volume of surface water compartment is generally not attempted in exercises designed for purposes of validating aquatic fate and transport models. Costs associated with obtaining quantitative groundwater flow data for such purposes are normally prohibitive. However, if considerable historical data are readily available for the study site or if the means of gathering current data exist (e.g., wells suitable for sampling are already present) and the model in question can accept such data, groundwater data could be included as an additional dimension to the model validation program.

Darcy's law can be used for determining rates and quantities of water moving in a large sand and gravel aquifer as follows:

$$Q = KA\frac{dh}{dt}$$

where: $Q$ = Discharge

$K$ = The coefficient of permeability

$A$ = The cross sectional area of the aquifer

$\frac{dh}{dt}$ = The hydraulic gradient (Todd 1959).

K is derived mathematically from data collected from pumping a well while using observation wells to define the drawdown curve.

The feasibility and necessity of attempting to obtain groundwater data should be carefully evaluated before the decision is made to incorporate these data into aquatic fate and transport models. If, after all factors are considered, such efforts can be justified, the investigator should consult Appel (1980), Stettman (1971), and Reed (1980) and references cited therein for procedural guidance.

### Interflow ($M^3$/h)

Water that infiltrates the soil surface and moves laterally through the upper soil horizon and enters a stream channel without reaching the water table is known as interflow or subsurface flow (Linsley et al. 1949). The significance of interflow contribution to the total volume of streamflow varies widely from area to area depending upon soil types and rainfall rates. Considerable differences of opinion exist among hydrologists regarding the qualitative breakdown between groundwater and interflow. Because of the poorly defined nature of interflow and problem associated with the measurement, interflow and groundwater are sometimes considered as a single component of the hydrograph, while surface water is considered as the other component (Linsley et al. 1949).

For purposes of validating aquatic fate and transport models for toxic organic substances, interflow is best considered as a component of groundwater. Unless extensive data are available for a particular study reach where testing is to be conducted, interflow along with groundwater and nonpoint source surface runoff are best treated as a composite gain to streamflow between upstream and downstream boundaries.

### Nonpoint Source Water Volumes ($M^3/h$)

The volume of water and associated pollutants contributed to a water compartment via nonpoint sources are difficult to quantify owing to nonspecific (diffuse) nature of nonpoint source contributions. In many watersheds, contributions to waterways from nonpoint sources are negligible except during periods of rainfall when surface runoff may be substantial. To minimize factors associated with episodic nonpoint source contributions, selection of the study area is of vital importance. Potential contributing sources should be avoided to the extent possible in the event of a significant precipitation event. Such sources would include stormwater drains, runoff from roadways and paved surfaces such as parking lots, drainage ditches, and culverts. If it proves impossible to avoid all sources of nonpoint contributions to a compartment, the volumes of nonpoint source contributions plus groundwater and interflow can be computed by determining differences in discharges between upstream and downstream compartment boundaries, and factoring out point source and tributary stream inflow contributions. Assuming no substantial loss from the compartment occurs as a result of diversion, withdrawals, etc., the increases in volume at the downstream boundary of the compartment can be attributed to the collector influences of nonpoint sources groundwater and subsurface flows (interflow).

### Tributary Inflow ($M^3/h$)

The volume of water entering a water compartment via tributary streams can be calculated or measured following procedures described in the Streamflow section below.

### Streamflow Entering Compartment ($M^3/s$)

Streamflow is defined as the discharge in a natural channel (Langbein and Iseri 1960). Discharge is the volume of water that passes a given point within a unit of time. Stream discharge values are normally reported in units of cubic meters per second ($M^3/S$ - SI units) or in cubic feet per second (CFS - English units).

A value for stream discharge at a site can be obtained: 1) from established stream gaging stations; 2) by installing a staff gage and establishing a rating curve for the reach; or 3) by on-site measurement at the time of sample collection.

## Established Gaging Stations

The most desirable approach is to locate the sampling site near an established and operational stream gaging station. Most such stations within the United States are operated by the United States Geological Survey (USGS). Although, in general, only mean daily discharge values are published, instantaneous or at least mean hourly discharge values with a known error band can be obtained by contacting the servicing USGS office. Many gaging stations are also used as USGS water quality monitoring sites and thus an historic water quality record may exist. Information on site selection, development and operation of USGS gaging stations is given by Carter and Davidian (1968), Buchanan and Somers (1968), and Buchanan and Somers (1969). Location data and flow records are published on an annual basis for the individual states by the USGS in cooperation with each state. These documents have the general title, "Water Resources Data for (state name) - Water Year 19__."

## Installation of Staff Gages

If a stream gaging station is not available or the sample collection site cannot be located at a gaging station for other reasons, it may be desirable to install a simple stage measurement (staff) gage and develop a rating curve or stage-discharge relationship for the site. Due to the effort involved, this approach should be considered only if a long term (years) sampling program is to be maintained and a very stable channel with good channel control exists at the site.

The methodology for developing a stage-discharge relationship is described briefly in the following paragraphs. It is in essence the same approach as used to establish a stream gaging station except that automatic water level recording equipment would be incorporated in a permanent gaging installation. Detailed descriptions of these procedures are included in Carter and Davidian (1968) and Buchanan and Somers (1968).

A stage-discharge relationship is an expression of the correlation (mathematical or graphical) between gage height (stage or depth of water) and discharge at a point on the stream channel. Development of a reliable stage-discharge relationship requires careful selection of the channel reach. The reach should be relatively straight and stable; that is, not prone to significant channel shifts or cutting and filling under different flow regimes. In addition, a good channel control should exist at the outflow end of the reach. An example of natural control would be a solid rock channel bottom or constriction; artificial control would be provided by concrete bridge abutments, broad crested weirs, etc. The purpose of channel control is to assure that the stage-discharge relationship will not be significantly altered over time due to major channel downcutting, aggradation or by bank erosion causing consequent channel shifts or size changes.

Once the channel segment is selected, a simple water level or staff gage is installed near the stream bank. This allows visual determination of the elevation of the water surface above some arbitrary datum. Discharge measurements (described below) and corresponding gage readings are then taken under a variety of flow conditions until enough data pairs are available to define a graphical relationship. Subsequently, stream discharge values can be obtained for the site by simply reading the gage height and consulting the constructed graph.

An advantage of this approach is that in a long-term sample collection program a stream discharge measurement is not required at the time of each water quality sample collection. Disadvantages are: 1) the level of "upfront" effort involved, 2) the low probability that a stable channel and channel control will be available at a desired water quality sampling site; and 3) the inherent deficiencies of stage-discharge relationships at flow extremes which result in significant errors in estimated discharge values under very low or high flow conditions.

On Site Measurements

In the majority of cases where permanent gaging station data are not available it will be necessary to physically measure stream discharge at the time of sample collection. This can be accomplished by current meter measurements on the majority of streams, or by installation of portable weirs or flumes or by volumetric measurements on very small streams.

The basic instruments for current or stream velocity measurements are the Price and pygmy meters. Both of these current meters are basically structured as cup-type bucket wheels moving on vertical shafts with bearings that operate in air pockets. The Price meter is appropriate for deep and swiftly flowing streams, being accurate at velocities up to 6 meters per second (20 fps). The smaller pygmy meter is accurate at much slower velocities and will function in streams as shallow as 0.06 meters (2 to 3 inches). Standard procedures for the operation and maintenance of both meters are given in Buchanan and Somers (1969) and Smoot and Novak (1968).

The procedures followed in making current measurements are similar for both types of meters. For very deep and swiftly moving streams the measurements with a Price meter must be conducted from a secured boat or from bridges or other structures spanning the stream. In streams that can be safely traversed by wading, the meter (Price or pygmy) is attached to a hand-held wading rod. A great variety of ancillary equipment is necessary for meter operation, especially in the case of non-wading measurements. A description of the various equipment options and functions is beyond the scope of this discussion but is adequately covered in Buchanan and Somers (1969).

The discharge measurement itself is a summation of the products of partial areas of stream cross sections and their respective average velocities or

$$Q = (av)$$

where:

Q = Total discharge

a = An individual partial cross section area

v = The mean velocity of flow for the area as measured by the current meter.

To conduct a discharge measurement, a relatively straight reach of stream should be identified which is free of debris and other flow interferences. Near the middle of this reach a cross section is selected and by use of a steel tape or other measurement device is divided into segments of equal width. The USGS recommends at least 20 segments if feasible; very small streams would be the obvious exception. At the midpoint of each segment the water depth is measured and the flow velocity is determined with the current meter. When all segments in the cross section have been measured they are summed to produce a value for total stream discharge. Again, this has been a very simplified description addressed more to the concept than to actual procedures. A comprehensive description of equipment and standard USGS procedures for making discharge measurements is given in Buchanan and Somers (1969).

Discharge of small streams ($<0.1\ m^3/s$), which are too shallow or slow moving for reliable current meter operation can be obtained relatively easily and quickly by use of portable weirs or flumes or by volumetric measurement. Small 90 V-notch weirs can be easily fashioned from 10- to 16-gauge sheet metal. If properly used, such a weir with a 1-foot deep notch will measure flows from 0.006 to 0.07 m3/s (0.002 to 2.5 CFS) within 3% accuracy. Small modified Parshall flumes made from lightweight aluminum are available commercially. They are easier to install than weirs and provide comparable accuracy over a flow range of 0.00003 to 0.014 $m^3/s$ (0.001 to 0.5 CFS). Both devices are installed by placing them within the stream channel, and carefully leveling and damming the remaining channel so that all flow is diverted through them. Measurements are taken by determining the head or depth of water passing through the rated control section (weir notch or throat of flume). Discharge values are then obtained from published rating tables. In very small streams, where the total flow can be diverted into a bucket or other container of known capacity, the discharge rate can be determined volumetrically. This "bucket and stopwatch" approach is fairly self-explanatory. Detailed descriptions of portable weir and flume installation, operation, and measurement and of the volumetric method are provided in Buchanan and Somers (1969) and U.S. Bureau of Reclamation (1967).

### Nonpoint Source Sediments Entering Compartment (kg/h)

Quantification of NPS sediment loading to stream compartments is at least as difficult as determining the volumes of water contributed by NPS. By far, the preferred method of dealing with NPS sediment contribution for purposes of validating specific fate and transport models is to avoid stream reaches and watersheds with a high potential for NPS sediment contribution. Sediments entering streams, regardless of their origin, are incorporated into, and transferred between both sediment and water compartments. Naturally, the finer sediments with slower settling rates are more likely to remain as components of the water compartment than the coarser, heavier materials.

Potential nonpoint sources of stream sediments are prevalent in most watersheds, thus, it is not always possible to select study reaches that are immune from sediment influences. Careful surveillance of possible study sites with an eye toward minimizing effects of sediment input, particularly during periods of heavy rainfall and high discharge, can greatly reduce the complicating effects introduced by sediments. Major contributing sediment sources should be avoided if possible; these include: 1) stream reaches with large expanses of easily erodable, exposed, stream banks comprised largely of unconsolidated soils; 2) recently tilled agricultural lands especially those planted to row crops with little or no buffer zone (green belt) along the stream; 3) areas of disturbed landscape such as ongoing housing development projects, logging operations, road construction, mining activities including unstabilized spoil areas, roadways and parking lots; and 4) in western states, particularly, areas of denuded landscape resulting from overgrazing and the generally sparse nature of vegetation. If the study reach selected is subject to nonpoint source sediment influences, it may be possible to estimate the quantities of sediment introduced to the stream. Subsequent sampling within the stream may yield sufficient data to permit computation of the quantities of sediments in the bedload, in bed material, and in suspension in the water column.

Nonpoint sediment yield can be estimated using equations developed for specific application. The U.S. EPA (1973) and McElroy et al. (1976) discuss sediment prediction methods for various agricultural sources. Also, a number of individual papers using predictive methods are compiled in the proceedings of the third Federal Interagency Sedimentation Conference of the Water Resource Council (1976).

Although the majority of sediment loading functions have been developed primarily for application to cropland, some, e.g., the Universal Soil Loss Equation (USLE), have application to non-cropland and to some extent to silvicultural, construction, and mining activities (McElroy et al. 1976). The U.S. EPA (1973) and McElroy et al. (1976) provide sufficient information to decide the feasibility computing NPS sediment loading functions for a particular situation, and to select the most appropriate model. The investigator should be well aware of the potential for introducing errors as a result of incorporating data derived through mathematical computations into aquatic fate and transport models.

### Tributary Sediment Inflow (Kg/h)

The amount of sediment entering stream compartments per unit time via tributary inflow can be determined following procedures described for sediment sampling within compartments. The sampling site is established near the mouth of the tributary stream in question and the total quantity of suspended and bedload materials are computed. It is assumed that all materials in transport at the mouth are discharged to the receiving stream. Owing to differences in flow velocities, total volume of flow, gradient, etc. between tributary streams and the main receiving stream, the percentage distribution of contributed suspended and bedload sediments will not necessarily remain consistent from tributary stream to the main channel. That is, a large percentage of sediment in transport as bedload in the tributary stream may become suspended components of the water column upon entering the main channel. Consequently, extrapolation of percentage distribution of sediment data from tributary to mainstream is not necessarily valid. Sediment measurements should be made within the stream compartment to determine the distribution of total sediments between the water column, bedload and stream bed materials.

### Suspended Sediments

The amount of suspended sediment entering a stream sampling compartment or reach is determined by the same procedures as described for suspended-sediment discharge. The sample site will, by definition, be located at the upstream boundary of the sampling compartment. To produce a value more appropriate for comparison with other water quality variables measured in the compartment, the suspended sediment discharge may be computed in units of kg/hour (tons/hour) or kg/min (tons/min). This requires mean hourly or instantaneous stream discharge values for the rate calculations.

### Bedload Sediment

The amount of bedload sediment entering a stream water quality sampling compartment or reach is best determined by the same computational procedures as described for bedload sediment discharge. The stream cross section for data collection will, by definition, be located at the upstream boundary of the sampling compartment. The bedload sediment discharge values may be computed in units of kg/hour (tons/hour) or kg/min (tons/min) to allow for meaningful comparison with instantaneous measures of water quality that may be obtained within the stream compartment.

### Biota

Living organisms, both aquatic and non-aquatic, are continuously entering and leaving water and sediment compartments. The biota are integral components of aquatic ecosystems and their role in contributing, dispersing, transforming, and removing organic pollutants to, within, and from ecosystem compartments is substantial. Procedures for obtaining biomass measurements in aquatic system are discussed at length in Appendix B.

## PARTICULATE ORGANIC MATTER

Like the biota, nonliving particulate organic matter is a component of all natural aquatic systems serving as an attachment surface and transport mechanism for pollutants with sorptive tendencies. Particulate organic matter in water and streambed sediment is typically measured by weight loss through ignition at 550°C of previously dried and weighed samples. The organic contribution to the total sample is expressed either as a percentage of the total dried sample weight or in absolute weight per volume (e.g., mg/l water) or wt per wt (e.g., mg/kg sediment) values. Procedures for handling and analyzing water samples for measurement of particulate organic matter (volatile residues) are provided in APHA (1980) and U.S. EPA (1974). Methods for collecting and analyzing sediment samples for determining the organic factor are provided in this report under procedures for measuring percent organic matter in bed material.

## MEASUREMENTS WITHIN COMPARTMENTS

### Suspended Sediments

Suspended sediment is that portion of the total stream sediment load that stays in suspension for appreciable lengths of time. Suspended-sediment discharge is the quantity of suspended sediment passing through a given stream cross section per unit of time. This discharge is usually expressed in units of kilograms per day (Kg/D-SI units) or in tons per day (T/D-English units). The procedure for determining suspended-sediment discharge can be considered in the following segments: 1) site selection; 2) sample collection; 3) determination of concentrations; and 4) discharge calculations. Each of these components is discussed individually in the following paragraphs.

### Site Selection

Stream discharge is required to calculate the suspended-sediment discharge; therefore, the site would ideally be located at or near a gaging station. If this is infeasible, then an actual measurement of stream discharge will be required concurrent with collection of the suspended-sediment sample. Other site criteria are:

a. uniform channel with no major flow restrictions;
b. stable banks which are not being actively eroded;
c. lack of significant eddies or backwater effects;
d. lack of significant tributary inflows immediately upstream; and
e. existence of a bridge or other base for sampling if the stream is not wadable. This latter criterion often conflicts with the desirability of not having major flow restrictions in the channel.

### Sample Collection

Collection of suspended-sediment data requires a sampling device that will obtain a sample representative of the water-sediment mixture moving in the stream in the vicinity of the sampler. In addition, the sampler must be capable of collecting a composited vertical profile of streamflow. Vertical profiling is necessary because of the gravity effect on suspended sediment which causes fines to predominate in the upper levels of streamflow and coarser material near the stream bottom.

Several types of sediment sampling devices which meet the above criteria have been developed. For the purposes considered in this report, only standardized suspended-sediment samplers used by the USGS should be employed. Two major types are available: depth-integrating and point-integrating. Depth-integrating samplers collect and accumulate a sample as they are lowered to the bottom of the stream and raised back to the surface. The sampler must be moved at a uniform rate in a given direction but not necessarily at equal rates in both directions. Sampling depth is limited to approximately 4.6 meters (15 feet). The point-integrating sampler can be operated to obtain a depth-integrated sample in deep streams by manually opening and closing a sampling valve to integrate the stream depth in parts.

Both types of samplers are basically a streamlined metal casting with a hollowed interior for the sample container. An opening for interchangeable nozzles is located at the front of the samplers and leads to the internal sample container. Openings for air-exhaust from the sample container are also provided. The standard sample container is a 473 ml (1-pint) glass "milk" bottle. For certain sampling conditions a 946 ml (1-quart) sample bottle is used. The samplers are available in a variety of sizes and weights, the use of which is dependent upon stream conditions. The small and lightweight models are appropriate for sampling in wadable streams. The larger models, which weigh up to 91 kg (200 pounds), are used for cable-suspended sampling from bridges of very deep and/or fast moving streams.

A detailed description of suspended-sediment samplers and sampling procedures is contained in Guy and Norman (1970) and Vanoni (1975). The major concern in sampler operation is to move the sampler at such a rate that the sample container becomes filled, or nearly so, just at the end of one or more vertical sampling trips. The major deficiency of existing samplers is their inability to collect a sample of water-sediment mixture near the streambed. A zone within 9 to 15 cm (3.5 to 6 inches) of the stream bottom is not sampled because of the need to keep the sample nozzle out of the bottom sediments. Coarse grained sediment is prevalent in this zone. Therefore, the concentration of suspended-sediment samples is usually lower than the true suspended-sediment concentration. For this reason the suspended-sediment discharge computed from samples is called measured suspended-sediment discharge.

Reliable determination of suspended-sediment discharge requires that the sample(s) be representative of the total stream cross section. The sampling methodologies to achieve this can range from simple to fairly complex. For streams with a stable channel and a uniform lateral suspended-sediment concentration, sampling at a single vertical will usually be adequate. However, the location of that "mean" vertical must be determined by trial multi-vertical sampling. For streams with unstable channels or with highly variable sediment loads, multi-vertical sampling (commonly 4 to 20 sites in a cross section) should be conducted at all times. Two general approaches for multi-vertical sampling are used by the USGS: 1) method of centroids-of-equal discharge increments (EDI) across the stream; and 2) method of equally spaced verticals across the stream with an equal sampling transit rate (ETR) at all verticals. A detailed explanation of these methods is contained in Guy and Norman (1970). Both methods produce results of comparable accuracy. The ETR method has an advantage in that the individual samples can be composited for laboratory analysis of suspended-sediment concentration. In addition, it is a more intuitive method which can be quickly and easily implemented by field personnel.

## Concentrations Determination

After field collection, samples are shipped to an appropriate laboratory for determination of suspended-sediment concentration. No special procedures for sample handling are necessary. The most important requirements are that the bottles be adequately sealed and labeled with detailed site and collection procedure information.

The common unit for expressing suspended-sediment concentration is milligrams per liter (mg/l). This is computed as one million times the ratio of the dry weight of sediment in grams to the volume of water-sediment mixture in cubic centimeters. Because it is more convenient to obtain the weight of the water-sediment mixture (the sample) than its volume, the following formula involving parts per million (ppm) is generally used.

$$\text{mg/l} = C \; \frac{\text{weight of sediment} \times 1{,}000{,}000}{\text{weight of water-sediment mixture}}$$

where: C is a variable adjustment factor that accounts for the fact that one mg/l is not equal to one ppm at concentration levels greater than 16,000 ppm.

Given the purpose of sampling considered in this report, only the mean suspended-sediment concentration for each stream cross section will be required. Therefore, a single composite sample can be analyzed rather than individual samples from all verticals. Samples collected by the EDI method can be composited only if individual sample volumes are equal; samples collected by the ETR method must be composited, either physically or arithmetically.

The two most common and accepted methods for determining the weight of sediment in samples are evaporation and filtration. The filtration method is faster but is not amenable to samples with high suspended-sediment concentration because of filter clogging. The evaporation method requires an adjustment for dissolved solids if the dissolved load is high in comparison to the sediment load. A detailed description of laboratory procedures for both methods is given in Guy (1969).

## Discharge Calculations

The basic method for calculating the average suspended-sediment discharge at a stream cross section is

$$Q_s = Q_w C_s k$$

where:

$Q_s$ = The sediment discharge in kg/day (tons/day)

$Q_w$ = The stream discharge in $M^3/S$ (CFS)

$C_s$ = The mean concentration of suspended sediment in the stream cross section in mg/l (ppm)

k = A coefficient to adjust units.

More complex and presumably accurate methods are available to compute suspended-sediment discharge. All methods are described in Porterfield (1972).

### Size Distribution

Size distribution of suspended sediment refers to the breakdown of a suspended-sediment sample into various size classes. The results are usually expressed as percentages or proportions by weight.

Suspended-sediment samples for particle size analysis are collected with the same equipment and in the same manner as samples for determination of suspended-sediment concentration and discharge. The same criteria, for site selection and single vertical vs. multi-vertical sampling, hold. Therefore, collection of duplicate bottles at each sampling vertical is recommended if both discharge and size distribution of suspended sediment are to be determined. Also, because the primary focus is on average particle size distribution for the entire stream cross section, multi-vertical samples collected in a cross section should be composited, when possible, prior to laboratory analysis.

There are two generally accepted methods for separation of suspended-sediment samples into size fractions--separation by sieving and separation according to fall velocity in still water. The size range of material that can be analyzed by the methods is different. Therefore, the anticipated size range and the sampling objectives must be considered to determine which individual or combination of methods is appropriate for a given sample.

Sieve analysis can be performed on either wet or dried sediment samples. The wet-sieve method is preferred. Sieving is limited to size classes coarser than a 0.0625 mm, which is material retained on a 250 mesh sieve. If the distribution of finer particles is desired, the residual from the 250 mesh screen must be analyzed by one of the settling velocity techniques described below.

Although sieves are available which will classify material up to 16-32 mm (coarse gravel), a standard sieve analysis will result in determination of the following size classes.

| Class Name | Size Range (mm) |
|---|---|
| Very fine sand | 0.052 - 0.125 |
| Fine sand | 0.125 - 0.250 |
| Medium sand | 0.250 - 0.500 |
| Coarse sand | 0.500 - 1.000 |
| Very coarse sand | 1.000 - 2.000 |

Results from a sieve analysis should be reported in percent to the nearest whole number. A detailed description of sample preparation is given in Guy

(1969). Standard ASTM procedures for conducting a sieve analysis should be followed and are described in ASTM (1938).

### Settling Velocity

A number of methods to determine particle size distribution based on differences in particle fall velocities have been developed. The methods recommended by the USGS are: 1) pipet; 2) visual-accumulation tube (VA tube); and 3) bottom-withdrawal tube (BW tube). Concentration of sediment in samples has a considerable effect on the accuracy of results. Prior to analysis, samples should be split or diluted to meet the following criteria.

| Method | Concentration in Tube (mg/l) |
|---|---|
| Pipet | 2,000 - 5,000 |
| BW tube | 1,000 - 10,000 |
| VA tube | total sediment not to exceed 12 cm of tube height |

The VA tube method is valid only for material in the size range 0.062 to 2.0 mm and thus is comparable to sieve analysis. The pipet and BW tube methods are valid only for sediments finer than a 0.062 mm. The following size classes will normally be determined by these methods.

| Class Name | Size Class (mm) |
|---|---|
| Coarse clay | 0.002 - 0.004 |
| Very fine silt | 0.004 - 0.998 |
| Fine silt | 0.008 - 0.016 |
| Medium silt | 0.016 - 0.031 |
| Coarse slit | 0.031 - 0.062 |

Results from all particle fall velocity methods should be reported in percent to the nearest whole number. A description of laboratory procedures for these methods is given in Guy (1969).

### Organic Matter

Organic matter in suspended sediment ranges from macroscopic plant material to microscopic colloidal humus. In the majority of streams, organic material will constitute a small percentage of total suspended sediment load. However, for certain water quality applications it may be important to know the actual amounts present. In addition, quantitative determination of organic content of suspended sediment is recommended for samples analyzed for particle size distribution by fall velocity methods. This is because of the effect the lower specific gravity organic material has on settling velocities. This issue is further discussed in Guy (1969).

Measurement of percent organic matter should be performed on additional duplicate bottles collected during sampling for determination of suspended-sediment discharge and particle-size distribution. The recommended methodology for quantifying organic matter content involves weighing of a dry sediment sample followed by removal of the organic matter and re-weighing of the remaining sediment. The weight percentage of organic matter is then determined by difference. Three techniques are available for removal of organic matter from a sediment sample: 1) hydrogen peroxide oxidation; 2) specific gravity separation; and 3) combustion. Laboratory procedures for each of the techniques are described in Guy (1969).

## BEDLOAD SEDIMENTS

### Discharge

For a variety of reasons, physical measurement of true bed load is difficult. First, many mechanical sampling devices, placed on or within the streambed, will decrease the velocity at the sampler and thus decrease the rate of bedload movement. Another major difficulty is that the velocity of water near the streambed varies greatly both in time and space. This results in bedload particles moving intermittently and at an average velocity which is much less than that of the stream flow. This behavior makes it very improbable that any given sample will be representative of long term conditions at the sample point or of conditions at other points in a stream cross section. More detailed explanations of the problems associated with bed load sampling are given in Guy and Norman (1970) and Hubbell (1964).

Despite these inherent problems, there is a long history of attempts to develop bed load sampling devices that would be reliable yet simple enough for field application. Many of the designs tested are described in Hubbell (1964). One of the most frequently used devices is the Helley - Smith (1971) pressure-difference sampler. Research is continuing, but to date no bed load sampling devices have been developed which are routinely used or recommended for use by the USGS.

In lieu of direct measurement, standard USGS procedures are to compute bed load movement or discharge through use of one of several mathematical formulas. The formulas in general use are based primarily on semi-empirical considerations of stream hydraulics and particle behavior. As such, a comprehensive description of the individual formulas is beyond the scope of this report. The methods are described in detail in Einstein (1950), Colby and Hembree (1955), and Colby and Hubbell (1961) and Brooks (1965).

The Einstein procedure (Einstein 1950) was developed in 1950 as a method for computing the total discharge of sediment of the sizes found in appreciable quantities in the streambed. The method is based on both theoretical considerations and experimental findings and requires hydraulic data from cross-sections within a reach and particle size data. A modified Einstein procedure was subsequently developed (Colby and Hembree 1955) which computes the total discharge charge of all particle sizes (the total sediment load) in the stream and requires a single depth-integrated suspended load sample. The formulas in the modified procedures are based on such easily measurable quantities as the concentration and particle size distribution of suspended sediment, the particle size distribution of streambed material, and the mean velocity of streamflow.

The basic equation in the modified procedure for computing the rate of bed load discharge (in tons/day) of particles of a given size range ($i_B Q_B$) is

$$i_B Q_B = i_b W (43.2)(1{,}200) D^{3/2} \phi/2$$

where: $i_b$ = the fraction by weight of the bed material in the size range

$W$ = the width of the stream, in feet

$D$ = the geometric mean size (the square root of the product of the upper and lower sizes of the range), in feet

$\phi/2$ = the intensity of bedload transport

As suggested by the equation, computations may be performed for several ranges of particle sizes and the results summed to achieve a value for total bed load discharge. To reduce this computational requirement, another version of the modified Einstein procedure has been developed which replaces many of the numeric calculations with graphical methods (Colby and Hubbell, 1961).

An earlier but widely utilized method for determining total bed load discharge per unit of stream width is summarized by the formula (DuBoys, 1879).

$$q_B = \Psi_d \tau_o (\tau_o - \tau_c)$$

where $q_B$ = bedload discharge, N/m-sec or $lb_f$/ft-sec

$\Psi^d$ = $0.17/d^{3/4}$ = bed-material discharge coefficient, $m^3$/N-sec or $ft^3/lb_f$-sec

$\tau_o$ = $\gamma HS$ = shear stress at the water-bed boundary, $N/m^2$ or $lb_f/ft^2$

$\tau_c$ = critical shear stress, $N/m^2$ or $lb_f/ft^2$

$\gamma$ = specific weight of the fluid, $lb_f/ft^3$

$d$ = median particle diameter, mm

$H$ = mean depth, m or ft

$S$ = energy slope, m/m or ft/ft

This procedure requires the following field data inputs: 1) the flow depth and slope; 2) characteristics of bed material, specifically the median particle diameter 3) the critical shear stress of the bed material; and 4) the specific weight of the transporting water.

Total Load

The total sediment load includes bed load plus suspended sediment load. Many formulas exist, including a modification of the Einstein method (Colby and Hembree, 1955), three formulas which have been calibrated with flume and field measurements (Engelund-Hansen, 1966, 1967; Inglis-Lacey, 1968; and Toffaletti, 1968, 1969).

The Engelund-Hansen formula requires field measurements on the specific weight of bed sediment, the mean stream velocity, the median diameter of bed sediment, the specific weight of the water, and the bed shear stress. It yields the total sediment discharge per unit width of stream.

$$q_t = 0.05\ \gamma_s\ u^2 \sqrt{\frac{d}{g(\gamma_s/\gamma-1)}}\ \left(\frac{\tau_o}{(\gamma_s-\gamma)d}\right)^{3/2}$$

where $q_t$ = total sediment discharge, lb/ft-sec
$\gamma_s$ = specific weight of sediment, $lb/ft^3$
$\gamma$ = specific weight of water, $lb/ft^3$
$u$ = mean stream velocity, ft/sec
$d$ = median bed particle diameter, ft
$\tau_o$ = bed shear stress, $lb/ft^2$
$g$ = gravitational constant = 32.2 $ft/sec^2$

This equation was calibrated with data from a very large flume (8 ft wide x 150 ft long) with sediments larger than 0.19 mm median diameter. The authors do not recommend it for use on fine bed materials, less than 0.15 mm.

The Inglis-Lacey formula relates total sediment discharge to the mean velocity of the stream to the fifth power.

$$q_t = 0.562\ \frac{(\upsilon g)^{1/3}}{w}\ \frac{u^2}{gH}\ \frac{\gamma u^3}{g}$$

where $q_t$ = total sediment discharge per unit width, lb/ft-sec

$\upsilon$ = kinematic viscosity of fluid, ft 2/sec
$u$ = mean stream velocity, ft/sec
$g$ = gravitational constant = $ft/sec^2$
$H$ = flow depth, ft
$\gamma$ = specific weight of water, $lb_f/ft^3$
$W$ = fall velocity of median size bed particle, ft/sec

This equation was calibrated with field data from large, stable irrigation canals.

Toffaletti (1968, 1969) divided the stream into four depth zones for the purpose of calculating a total sediment discharge. The bed sediment is divided into standard size fractions. Hydraulic quantities which are required include the temperature and viscosity of the water, mean stream velocity, hydraulic radius, energy slope, stream width, and bed shear velocity. The formula was based on extensive data from seven rivers and flume data from four investigators. Most of the transport was due to sand in these instances. To date, there is not a verified formula which describes total sediment transport of silts and clays.

## Size Distribution (%)

Size distribution of bedload sediment would be defined as the percentage breakdown of a bedload sediment sample into various particle size classes. However, as discussed in the section of this report on determining bedload discharge, obtaining representative samples of true bedload is improbable at best. For this reason, size distribution analysis of streambed sediments are normally performed on samples of what is termed "bed material." Bed material is defined as the mixture of streambed sediment that is exposed to the errosive force of flow and which can, or may move during any relatively short period of time. This material is located from the surface of the streambed to a depth of approximately 3 to 20 cm (1 to 8 inches). Bed material and bedload are not synonymous. Bed material will normally be coarser grained than true bedload and the exclusion of the finer grained sediments that may bounce or roll along the bed.

Three basic types of bed-material samplers are recommended and used by the USGS: 1) vertical; 2) rotating bucket and scoop; and 3) surface samplers. Details of design and operation of these samplers are contained in Guy and Norman (1970).

Vertical samplers consist of a hand-held cylindrical tube which is forced into the streambed and retrieved with the sample core retained by suction. Collection of a sample up to 15 cm (6 inches) in depth is possible in fine grained bottom sediments. However, only the top 25 mm (1 inch) of sample is normally retained for particle size analysis. This procedure is followed to make the sample more closely representative of true bedload.

The rotating bucket scoop sampler is available in two different size-weight configurations for varied stream depth and/or velocity conditions. Both models are designed for cable-suspended sampling of non-wadable streams. They consist of a streamlined metal bomb with a spring loaded rotating scoop built into the bottom surface. When the sampler encounters the streambed, the scoop is released and rotates around and upwards into the body of the sampler. Both models sample to a depth of about 50 mm (2 inches). All of the sample must be retained for particle-size analysis because of the mixing which occurs during the scooping process.

The streambed surface sampler used by the USGS consists of a small circular disk filled with petroleum jelly mounted on the bottom of a cable-suspended sounding weight of appropriate size for stream flow and depth conditions. Upon contact with the streambed, the surface particles adhere to the jelly. The sample is then retrieved and sent in a sealed container to a laboratory where the sediment is separated from the jelly.

It should be noted that all of the described samplers are designed to recover particles in the silt to coarse sand size range. Effective sampling of larger particles (gravel, cobbles, and boulders) is difficult and no reliable mechanical sampler exists. The need to consider these larger particles should be evaluated for each individual site in view of sampling program objectives. If a sample is required, gravel and larger material may be collected by scoop sampling or manual picking within a measured area large enough to provide a representative sample. There is no acceptable methodology for sampling coarse particles in non-wadable streams.

Standard containers for storage and transport of samples from all of the described mechanical or manual sampling methods are wide-mouthed plastic bottles or waxed cardboard containers. No special sample handling procedures are necessary beyond assuring that the containers do not leak or spill during transit.

Procedures for bed-material sampling for particle size analysis are comparable to sampling procedures for suspended sediment. Basically, a sufficient number of individual verticals or sites must be sampled on a cross section to adequately represent the distribution of particle sizes over the entire channel. A large number of individual samples (5 to 15) may be appropriate in an unstable mixed silt, sand, and gravel channel. Depending upon channel width, 3 to 5 individual samples may be adequate for streams with fairly stable and homogeneous bottoms. The depth of samples taken at all individual sites within a cross section should be constant. Following sample collection, individual samples may be composited or analyzed for size distribution separately, depending upon the objectives of the data collection program.

### Organic Matter in Bed Material

Measurement of the amount of organic matter in stream bed material should be performed on a set of duplicate samples collected concurrently with those for determination of particle size distribution. Equipment and procedures for collection of these samples are outlined in the preceding section of this report.

The recommended methodology for quantifying organic matter content involves weighing of a dry bed-material sample followed by removal of the organic matter and re-weighing of the remaining sediment. The weight percentage of organic matter is then determined by difference. Three techniques are available for removal of organic matter from the sediment sample: 1) hydrogen peroxide oxidation; 2) specific gravity separation; and 3) combustion. Laboratory procedures for the listed techniques are described in Guy (1969).

### Bulk Density ($g/cm^3$)

Bulk density of soil (or sediments) is the ratio of the mass to the bulk or macroscopic volume of soil particles plus pore space in a sample (Black et al. 1965). The mass is determined after drying to constant weight at 105°C, and the volume is that of the sample as collected in the field. For sediment samples in which the void spaces are saturated with water, W, density, D, is expressed as the ratio of the mass (both solids and water) for a unit volume, V, of sediment (Guy 1978).

Thus, $D = \frac{W_s + W_w}{V}$

Where D = Density

$W_s$ = Mass of dried soil or sediment (g)
$W_w$ = Mass of water (g)
$V$ = Total volume ($cm^3$).

## Water Content

Moisture content of bottom sediment is determined by weighing a fresh sediment sample, drying the sample to a constant mass at 105°C-110°C and reweighing the dried sample (Guy 1978). Thus, percent moisture on a dry weight basis ($M_d$) is computed as follows:

$$Md = \frac{W_{ws} - W_{ds}}{W_{ds}} \times 100,$$

where: $W_{ws}$ = Mass of wet sediment

$W_{ds}$ = Mass of dry sediment.

Collection of samples for determination of moisture content follows procedures described for sampling the bedload and bed materials. Since the measure is based on loss of moisture through evaporation, the sediment sample must be stored in air tight container to prevent moisture loss.

## Biota

The biota associated with the streambed (benthic macroinvertebrates, periphyton, rooted aquatics) are important components of these ecosystem. Procedures for obtaining biomass measurements of these components of the community are described in the section on Bioconcentration and in Appendix B.

## WATER COLUMN

### Water Temperature (°C)

Water temperature measurements are determined following procedures described in the Biotransformation section.

### Dissolved Oxygen (mg/l)

Procedures for collecting, handling, and analyzing water samples for dissolved oxygen determination are described in the Biotransformation section.

### Dissolved Organic Carbon (mg/l)

Procedures for collecting, handling, and analyzing water samples for dissolved organic carbon determination are described in the Photolysis section of this report.

### Total Organic Carbon

Total Organic Carbon (TOC) is determined using procedures and materials outlined in APHA (1980), pp. 471-474. An infrared analyzer detects carbon concentrations of from 1 to 150 mg/l. Greater or lesser concentrations can be measured by appropriate dilution or concentration of samples. Because the carbon analyzer measures all carbon present in the sample, steps must be taken to separate the inorganic carbon. This is accomplished either by acid decomposition and volatilization of the inorganic carbonates prior to analysis, or, if the analyzer is equipped to measure carbonate and bicarbonate carbon, by direct measurement.

Water samples for TOC analysis should be collected and stored in glass bottles, preferably brown, and sealed with Teflon-lined caps. Samples should be analyzed promptly, but if delay is unavoidable, store samples at ice temperature with minimal exposure to light and atmosphere or acidify with hydrochloric acid to a pH not over 2 (APHA 1980).

### Biota

Procedures for obtaining quantitative estimates of the biomass associated with the water column (e.g., phytoplankton, fish, zooplankton, drift organism, floating and rooted macrophytes, etc.) are discussed in depth in the Bioconcentration section and Appendix B.

### Eddy Diffusivity ($M^2/h$)

Eddy diffusivity (turbulent diffusion) refers to mixing of dissolved and fine particulate substances due to micro-scale turbulence. Determination of eddy diffusivity is discussed in Berner (1980), Fisher (1979), Yotsukura and Cobb (1972), Yotsukura and Sayre (1976), Edinger and Geyer (1965), and Schnoor and Fruh (1979).

## LOSSES FROM COMPARTMENT SEDIMENTS

### Suspended Sediments

The amount of suspended sediment leaving a stream sampling compartment or reach is determined by the same procedures as described for suspended-sediment discharge. The sample site will, by definition, be located at the downstream boundary of the sampling compartment. If significant tributary inflows do not occur within the compartment and if the stream channel is stable, it may be assumed that the suspended-sediment discharge will be equal to that entering the compartment. If these conditions are not met, sampling at both upstream and downstream boundaries of the compartment may be appropriate.

### Bedload Sediments

The amount of bedload sediment leaving a stream water quality sampling compartment or reach is best determined by the same computational procedures as described for bedload sediment discharge. The stream cross section for data collection will, by definition, be located at the downstream boundary of the sampling compartment. If significant tributary inflows do not occur within the compartment and if the stream channel is stable it may be assumed that the outflow bedload sediment discharge will be equal to that entering the compartment. If these conditions are not met, separate determinations of bedload sediment discharge at both upstream and downstream boundaries of the compartment may be appropriate.

### Water Volume (Streamflow $M^3$/sec)

Procedures for determining the volume of water leaving a stream compartment are described under the Streamflow section. This determination is a total discharge measurement and is synonomous with the volume of water entering a compartment, except discharge is computed at the downstream compartment boundary.

### Biota

Living organisms are continuously in transit into, within and between compartments. Procedures for estimating the biomass lost through voluntary and involuntary movement are discussed in the Bioconcentration section and Appendix B.

### Particulate Organic Matter

Particulate organic matter associated with the stream and suspended in the water column is subject to bedload and streamflow movement through the compartment. Procedures for sampling and measuring particulate organic matter in transit are described in previous sections.

### Evaporation

Loss of water to the atmosphere may represent a substantial portion of the total water budget, particularly in waters of the southwestern U.S. Perez et al. (1974) point out that evaporation losses from surface water result in: 1) changes in concentrations of channel constituent due to changes in water volume; 2) losses of non ionic substances (e.g., ammonia); and 3) changes in the heat content which affects chemical and biological reaction rates.

Procedures for obtaining evaporation estimates in the field involve three phases (Perez et al. 1974): 1) Pan evaporation losses are measured and recorded; 2) the basic wide evaporation losses are estimated from measured values of all other variables in the water budget; and 3) a pan coefficient (proportionality factor) is found that will best relate the two results (Thornthweite and Mather 1955, Eagleson 1970, and Kohler 1954).

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## POLLUTANT LOADING INPUTS

Pollutant loading inputs to aquatic fate and transport models are summarized in Table 2-2.

### POINT SOURCES

The most conspicuous and easily measured sources of pollutant loads to aquatic systems are point source discharges confined to pipes that lead directly to the receiving water body. Computation of loading rates for such discharges is generally straightforward since the volume of flow in a discharge pipe and the concentrations of pollutants are relatively easily measured. Generally, considerable diurnal variability in both the volume of flow and pollutant concentrations is evident in municipal and industrial discharges owing to man's daily schedule of peak daytime activity interrupted by periods of reduced activity during the night. Consequently, it is common practice to calculate an average loading rate based on flow and pollutant concentration measurements taken over a 24 hour period. Such loading rates are generally expressed in pollutant mass per unit time (e.g., kg/h or kg/d). Obviously, loading computations based on a single instantaneous measurement will generally differ considerably from those based on daily mean values.

For purposes of aquatic fate and transport model validation studies, it is essential that a distinction be made between loading values based on instantaneous measurements and those based on daily, weekly or other mean values. This holds whether 1) the discharge is the primary source of the toxic organic pollutant whose fate and transport is being assessed in the model, 2) the discharge is a minor contributing source of the pollutant, or 3) the discharge is contributing an agent that tends to alter the activity, availability, concentration or other chemical characteristic of the pollutannt in question.

It is also important to observe the manner in which a discharge is assimilated by the receiving stream and to note any variability in dispersion rates and patterns that may occur through time. Considerable variation in mixing rates and boundaries of mixing zones is common in receiving waters whose flow is regulated by dams, diversion, withdrawal and return flows, or which experience considerable diurnal variability in the temperature regime as a result of periodic thermal or hypolimnetic discharges or natural temperature fluctuations. Also, the mixing patterns of the effluent containing the pollutant of study, may vary considerably depending upon the volume of the discharge, the chemical composition and temperature of the effluent.

These factors must all be considered in selecting a study area and designing an aquatic fate and transport model validation study for toxic organic substances. For further information on sampling program design and delineation of mixing zones for streams receiving regional wastes, the reader is referred to National Academy of Sciences (1973) and Fetterolf (1973).

## STREAMFLOW

Procedures for computing pollutant loads entering a designated reach or stream compartment are straightforward if the system is well mixed and the channel is relatively uniform and straight. The total discharge (Q) entering the upstream compartment boundary is calculated following procedures described in the Physical Transport section under the heading of Streamflow Entering Compartment. Sufficient samples are collected and analyzed to provide a mean concentration value (C) for the pollutant in question. Thus,

$$Y = KCQ$$

where: $Y$ = The pollutant load (kg/h)

$C$ = The mean pollutant concentration at the upstream compartment boundary (mg/1)

$Q$ = The discharge ($m^3/s$)

$K$ = A coefficient to adjust the units.

## SUSPENDED AND BEDLOAD SEDIMENTS

Procedures for computing the loading rates of sorbed pollutants to stream compartments via suspended and bedload sediments involve the same concepts as streamflow loading determinations. The total quality of both suspended and bedload sediments entering a stream compartment are determined following procedures described in the Physical Transport section. Mean concentrations of sorbed pollutants associated with the respective sediment functions are determined and loading rates computed for each as follows:

For suspended sediments: $Y_{SP} = Q_S C_{SP} K$

where: $Y_{SP}$ = The total pollutant load associated with suspended sediment (kg/h)

$Q_S$ = The mean suspended sediment discharge (kg/d)

$C_{SP}$ = The concentration of pollutant associated with the suspended sediment (mg/kg)

$K$ = A coefficient to adjust units.

For bedload sediment: $Y_{bP} = q t C_{bP} K$

where: $Y_{bP}$ = The total pollutant load associated with the bedload discharge (kg/hr)

$q_t$ = The bedload discharge (kg/d)

$C_{bP}$ = The concentration of pollutant associated with the bedload (mg/kg)

$K$ = A coefficient to adjust units.

## BIOTA

Loading of pollutants associated with and transported by the biota is computed by: 1) sampling the particular community component of interest following procedures described in the Biological Uptake section and Appendix B-1, 2) determining the total biomass of the appropriate community component in transit, 3) determining mean pollutant levels in tissues of each community of interest, and 4) computing the total pollutant load ($Y_B$) delivered to a compartment via the biota or biological component. Thus, $Y_B = C_B BKL$;

where: $Y_B$ = The total pollutant load transported to a particular compartment by the biota (kg/hr)

$C_B$ = The mean concentration of pollutant in biological tissue (mg/kg)

$B$ = The total biomass delivered to a compartment (kg/h)

$K$ = A coefficient to adjust units.

## PARTICULATE ORGANIC MATTER

Measuring the amount of particulate organic matter in suspended and bedload sediments for purposes of determining concentrations of associated pollutants must be accomplished through the specific gravity separation process following procedures described by Guy (1969). Computations of loading rates of sorbed pollutants associated with particulate organic matter are subsequently determined as follows:

$$Y_{POM} = C_{POM} Q_{POM} K$$

where: $Y_{POM}$ = The total pollutant load associated with particulate organic matter (mg/hr)

$C_{POM}$ = The mean concentration of pollutant associated with particulate organic matter (mg/kg)

$Q_{POM}$ = The quantity of particulate organic matter the compartment (kg/m)

$K$ = A coefficient to adjust units.

## GROUNDWATER

Some aquatic fate and transport models are designed to accept data on pollutant loading to surface waters via groundwater flow. Typical pollutant sources that would contribute such loadings are hazardous waste dumps, holding ponds, and soil contaminants that have percolated or leached into groundwater. Theoretically, such sites can be used as pollutant sources for verification of models, but from a practical aspect, direct quantification of such sources is infeasible.

Darcy's law is quite simple and can be used for determining rates and quantities of water moving in large aquifers composed of sand and gravel. However, application of the formula for an area of relatively small size, such as at a waste disposal site, is very difficult. The formula is:

$$Q = KA \frac{dh}{dt}$$

where $Q$ = The flow rate

$K$ = The coefficient of permeability

$A$ = The cross-sectional area

$dh/dt$ = The hydraulic gradient (Todd 1959).

K is mathematically determined from data collected by drilling and pumping a well while using a couple of observation wells to define the draw down curve. The cross-sectional area is also difficult to determine because height of the aquifer contributing to surface water recharge is unknown. It is possible for groundwater to flow upward into a streambed. The hydraulic gradient is more easily determined and only requires drilling about 3 wells to measure the change in height of the water table over distance. These measurements and Darcy's formula can be used to estimate groundwater flow to a surface water body.

To quantify the pollutant loading to surface water, however, it is also necessary to determine the average pollutant concentration in the groundwater. This can be done by drilling and sampling a series of wells in the contaminated aquifer but determining the depth to drill is again a problem.

The foregoing is not intended to indicate that waste dumps and ponds cannot be used as pollutant sources for model verifications. Such sources can be used but the suggested approach (for flowing waters) is to sample the cross-section of the river at a point downstream from the source. Depending upon the mixing in the river, it may be necessary to take a series of depth and flow integrated samples to obtain a precise loading estimate. Using this approach, the model loading is the pollutant load of the river, just upstream from the first compartment.

The use of groundwater flow as a source of contamination has one major advantage over many other sources. Groundwater loading rates are relatively steady compared to loads from effluents, atmospheric deposition and non-point source runoff. This steady type of input probably approximates steady state better than most uncontrolled sources.

## ATMOSPHERIC DEPOSITION

An important source term or input loading factor for particulate matter in a body of water is atmospheric deposition. Two primary mechanisms may contribute to the total load: dry deposition and wet deposition including rainout and washout. We can begin by defining the deposition velocity Vg

$$Vg = -\frac{J}{C} \tag{1}$$

where Vg has units of centimeters per second (cm/sec). J is the flux of material to a surface in nanograms per square centimeter per second ($mg/cm^2/sec$), and C is the atmospheric concentration in nanograms per cubic centimeter ($mg/cm^3$). The flux is assumed to be constant with height above the surface although C and Vg are functions of height.

Flux and concentration are related by:

$$J = (D + E)\frac{dC}{DZ} - VsC \tag{2}$$

where D and E are the Brownian and Eddy diffusivities, respectively, in square centimeters per second ($cm^2/sec$), Z is the height above the surface in centimeters (cm) and Vs is the sedimentation velocity in centimeters per second (cm/sec). The sedimentation velocity of a particle is reached when the aerodynamic drag force on a falling particle exactly balances the gravitational force. The minus signs are necessary since the flux downward to a surface is a negative quantity by convention and the deposition velocity is defined as positive.

Equation (2) applies to both small and large particles. For very small particles, however, the sedimentation term is negligible. It is also assumed that D is very much less than E, except very close to the surface or when there is no wind. Therefore, for small particles, let $E = ku*Z$, and substituting in equation (2):

$$J = -\frac{EdC}{dZ} = -ku*\frac{ZdC}{dZ} = -ku*\frac{dC}{C(hrZ)} \tag{3}$$

where k is von Karman's constant equal to 0.4, u* is the friction velocity in cm/sec, and hrZ is the natural logarithm of height.

For large particles, the diffusivities are negligible hence equation (2) reduces to:

$$J = -VsC \tag{4}$$

Comparison of equation (1) and (4) demonstrates that for large particles, the deposition velocity equals the sedimentation velocity. It should be mentioned that although equation (2) simplifies to equation (3) or (4) for small or large particles respectively, the general case has been examined by some researchers. For example equation (2) has been integrated by Chamberlain (1966) and shown in greater detail by Sehmel (1970), based on special assumptions concerning the form of E near the surface.

Several workers (Chamberlain 1966; Islitzer and Dumbauld, 1963; Sehmel 1972; Sehmel et al. 1973) have demonstrated that deposition velocities over rough surfaces are generally greater than sedimentation velocities for similarly sized particles. This effect is especially evident at high wind speeds. Impaction, turbulent deposition, and eddy diffusional deposition on the roughness elements are responsible for the high deposition rate when compared with sedimentation.

For a relatively smooth surface, Sehmel (1973) has shown that sedimentation may be controlling. In particular, Vg is shown to be equal to sedimentation velocity (Vs) for a wind speed of 2.2 meters per second (m/sec) for particles larger than 0.3 um in equivalent diameter. A smoother brass surface was used for this study.

Wet deposition processes include "rainout" or removal of pollutants from within clouds during precipitation events, and "washout" or below cloud scavenging. Some researchers believe that wet deposition is more efficient than dry deposition (Frantisak et al. 1980). However, the precipitation quality resulting from scavenging processes will vary from region to region and from storm to storm depending on the composition of the atmosphere at the time precipitation occurs.

Dry deposition is determined by sampling fallout on exposed surfaces of stainless steel or teflon for varying periods of time. Friedlander (1977) and Chamberlain (1960) provide standard methods for sampling both dry and wet deposition.

## NONPOINT SOURCE FLOW AND SEDIMENTS

As was pointed out in the discussion of nonpoint source flow in the Physical Transport section, the optimal means of dealing with nonpoint source contributions to water courses is to select study areas with minimal potential for nonpoint source influences. In the event nonpoint source flow, sediments and pollutant contribution cannot be avoided for whatever reason, the most cost-effective means of estimating the loading inputs is by treating all unaccountable increases in pollutant loads as nonpoint contributions, or as the collective contributions of nonpoint source, groundwater and interflow depending on the availability of data for the latter sources. The most probable cause of nonpoint contributions would be a precipitation event while the study is ongoing. The potential for contribution of toxic organic pollutants to the water body, depends on the nature of the watershed in terms of soil types, degree of slope, vegetative cover and, of course, its uses and quantities of mobile pollutants contained therein. Agricultural lands, for example, especially those dedicated to row crops, represent a potential source of organic pesticides that may be easily transported via overload runoff to a water course during an intense rainfall event. Similarly, mine tailings, dump sites, process waste piles and holding ponds from numerous industrial activities represent potential sources of a myriad of organic pollutant that could be mobilized by intense rainfall.

The investigator must be alert to the possibilities of such inputs both during the early surveillance stages of site selection as well as during the course of the study. Generally, visual observation (including aerial surveys) is the most efficient means of judging whether or not nonpoint contributions are of significant magnitude to warrant concern.

The use of loading models to estimate nonpoint contributions is generally not encouraged because it introduces another source of error to the total program. However, under some circumstances, this approach may be justified. For example, a number of watersheds have been intensively studied and modeled to examine the rates of pesticide movement from the field to water courses. In doing so, the hydrology, soil types, pesticide application rates, etc. have been sufficiently well described to permit good estimates of roles and routes of transport to receiving waters.

U.S. EPA reports by Crawford and Donigian (1973), McElroy et al. (1976), Haith and Loehr (1979), and Evans and Duseja (1973) will prove to be useful sources of information for persons interested in past efforts to evaluate non-point source loading contributions to surface water.

Procedures for determining through instream measurements, the nonpoint source contribution of pollutants that reach the water body compartments, whether transported by the waterflow or as sorbed components of the sediment, are essentially the same as those described previously for streamflow and suspended and bedload sediments; i.e., the quantities of pollutants in the respective compartment are determined at the upstream and downstream boundaries, and unaccountable increases in loading within the compartment is attributed to nonpoint pollutants.

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## SAMPLE COLLECTION, HANDLING, AND ANALYSIS FOR TOXIC SUBSTANCES

The previous sections on sampling have been primarily concerned with the collection of environmental input data that may be required for aquatic fate and transport models. Field validation of models also requires that the predicted outputs of a model (Table 2-1) be compared with actual field data. For these guidelines, it is assumed that the prime output of models being evaluated are concentrations of organic compounds in various media, i.e., fish, water, sediment, zooplankton, etc.

It is, however, beyond the scope of these guidelines to provide sample collection methods for all model outputs and then to provide sample preservation and analytical procedures for all organic chemicals that could be used in model evaluation. Most sampling procedures for water, sediment and biota have been described in previous sections (Bioconcentration and Physical Transport); however, special precautions are required during collection to avoid contamination or loss of organic pollutants. The "Handbook for Sampling and Preservation of Water and Wastewater" (U.S. EPA 1982) was developed for guidance on field monitoring required under the National Primary Drinking Water Regulation, The National Pollutant Discharge Elimination System, Section 304 (h) of the Clean Water Act, and the consent decree for priority pollutants. The handbook addresses the sampling of water and wastewater such as industrial/municipal wastewater, agricultural runoff, surface water, and sediments, as well as flow monitoring, handling and preservation methods. Extra attention is required to preserve the sample until the compound(s) of interest is extracted and analyzed. Individual investigators will have to identify the most appropriate sampling procedure based upon the projections of the model, the compound whose fate is being studied, and specific environmental factors at the study site. Prior to field sampling it is essential to precisely define the model's outputs.

Sampling procedures specific to priority pollutants are contained in "Sampling Protocols for Collecting Surface Water, Bed Sediment, Bivalves, and Fish for Priority Pollutant Analysis" (VERSAR Inc. 1982). This manual is currently in draft form but final publication is scheduled for 1984. Included in the document are sections on sampling ambient water, bed sediment and fish. All sections contain discussions of site selection, sampling equipment and use, and sample preservation and shipping. Container selection and cleaning are covered in the water and fish sections.

### REFERENCES TO ANALYTICAL METHODS FOR ORGANIC COMPOUNDS

Detailed analytical procedures have recently been proposed by the U.S. EPA (1979) for determining the concentration of 113 organic toxic pollutants in water. Methods 601-613 apply to the analysis of individual compounds or groups of chemically similar compounds. Methods 624 and 625 are GC/MS procedures for the analyses of the same compounds. The proposed methods cover calibration of instruments, quality control, sample collection, preservation and handling, sample extraction and analyses, and calculations. Revisions of the above methods appear in "Test Methods, Methods for Organic Chemical Analysis of Municipal and Industrial Wastewater" (Longbottom and Lichtenberg 1982). The majority of the revisions were made for clarification or to add additional flexibility for the analyst. Finalized procedures are to be published in the Federal Register in 1984.

Currently there are no EPA approved methods for determining priority pollutants in sediments or fish although the Environmental Monitoring and Support Laboratory in Cincinnati has prepared interim guidelines (U.S. EPA 1981). These procedures were originally prepared in 1977 and were revised in 1980 and 1981. Final guidelines will not be available until 1984.

Another source of analytical procedures is the "Analysis of Pesticide Residues in Human and Environmental Samples: A Compilation of Methods Selected for Use in Pesticide Monitoring Programs" (Sherman and Beroza 1980). Brief comments are addressed to the collection, preservation and storage of samples but the cleaning of glassware is covered in detail. A separate section is devoted to sampling analysis of water for pesticides with specific reference to free acid herbicides. Gas-liquid chromatographic procedures for the analysis of chlorinated hydrocarbon and organophosphorus pesticides in water are also covered.

These are but a few of the many references available for the determination of priority pollutants. Where possible, established methods should be used but this is not always possible or practical. Whatever method is selected, it must be tested and verified by the analyzing laboratory. For any EPA funded project, the laboratory must also prepare and follow a quality assurance plan.

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# APPENDIX A

# TIME AND DISTANCE CALCULATION

## APPENDIX A

## EXAMPLE OF TIME AND DISTANCE CALCULATION THAT THE COMPOUND OF INTEREST CAN BE DETECTED

### SAMPLE DESIGN

A sensitivity analysis of the EXAMS model using phenol in the Monongahela River predicts that phenol will only be detectable in water samples. Major factors to be considered in designing the water sampling program are:

1. Distance and time of water travel between phenol dischargers. Phenolic wastes are discharged at river mile (RM) 39.4 and no other significant phenol discharges occur until downstream of RM 23.8. The time of travel in the Monongahela River has been estimated by the U. S. Corps of Engineers (USCE). The water transit time between RM 39.5 to Lock 3 (RM 23.8) can be estimated by the following equation:

   $$V = aQb$$

   where: $V$ = Velocity in feet per second

   $a$ = correction coefficient (0.000196)

   $b$ = correction coefficient (0.92)

   $Q$ = River flow in cubic feet per second (CFS)

   The Monongahela River is regulated to maintain a minimum navigable flow (1,000 cfs) and climatic conditions control discharges above this level. The river flow on September 15 was approximately 4,000 cfs and was used as the best estimate of flow conditions for early October.

   Therefore:

   a) Velocity = $V = aQ^b = .000196(4000).92 = 0.04378$ ft/sec = 0.275 miles/hr

   b) Distance between the effluent discharge point and Lock 3 = 15.7 miles

   c) Time of travel = 57 hours

2. Concentration of phenol in Monongahela River below effluent. An estimate of 22.679 kg/day of phenol loading was obtained from the plant manager.

Loading

22.679 kg/day

(22.679 x $10^9$ µg/day)/(9.79 x/$10^9$/day) = 2.3 µg/l

River Flow

4000 CFS x 86400 sec/day x 7.48 gal/CF x 3.78 l/gal = 9.79 x $10^9$ l/day

3. Half-life of phenol in the Monongahela River.

Phenol degrades through bacterial breakdown and chemical oxidation.

Combined bacterial and chemical oxidation degradation rates have been estimated to be:

1.0 x $10^{-7}$ ml/cell/hr*

3.0 x $10^{-8}$ ml/cell/hr*

Average = 6.5 x $10^{-8}$ ml/cell/hr

Concentration of Bacteria in Monongahela River:

1.0 x $10^5$

1.0 x $10^6$

1.0 x $10^7$

Average = 1.0 x $10^6$ Cells/ml

T 1/2 = .693/K

where:

T 1/2 = half-life

K = site specific rate

0.693 = natural log of 2

T 1/2 = 0.693/(6.5 x $10^{-8}$) (1.0 x $10^6$) = 0.693/0.065 = 10.66 hours

4. Time and distance before phenol falls below minimum detection limit:

The following formula can be used to estimate time elapsed before phenol can be no longer detected:

$$c/co = e^{-kT},$$

where: $c$ = minimum detection limit (0.5 μg/1)

$c_o$ = concentration at outfall (2.3 μg/1)

$k$ = estimated rate of 6.5 x 10-2 per hour

$c/c_o$ = $0.5/2.3 = e^{-0.065\ T}$

$T$ = 23.5 hours

Therefore phenol can theoretically be tracked for about 24 hours or 6.5 miles based upon a flow of 4,000 cfs and a minimum detection limit of 0.5 μg/1.

*Normalize to the number of cells per ml of water estimated by standard plate count methods.

# APPENDIX B

# BIOCONCENTRATION METHODS

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## Appendix B-1. Description of Stream Habitats and Appropriate Macroinvertebrate Sampling and Processing Procedures.

### Pools--

Pools, or quiet waters, are usually found behind obstructions, in side eddies, or immediately downstream from riffles. The finest sediments (silts and finer) are deposited in pools, often along with considerable amounts of organic debris. Although the smallest proportion of the total substrate of a stream is pool-type substrate, the highest biomass per unit area is often found here. This is due to the stability of the substrate and the large amount of organic matter entrapped in the pools. The variety (diversity) of organisms found in pools, however, is normally much lower than is found elsewhere. In many cases, the greatest part of the biomass is represented by biting and non-biting midges and segmented worms.

If export of biomass through emergence is included in the model, it would be very useful and simple to separate the midges (which emerge) from the worms (which do not) while extracting the organisms from the samples. The most common sampling devices for use in pools include the Ekman grab sampler and coring devices described below.

Ekman Grab Sampler--This is probably the most widespread sampler used to sample soft (fine-particle) substrates. The sampler is lowered onto the substrate with jaws open and is triggered to close by a messenger if lowered by line, or through a specially built pole used for hand operation. As the sampler closes it grabs a fixed area of bottom substrate. The Ekman grab collects a fairly shallow sample and will thus miss organisms living several inches deep in the substrate. Weber (1973) lists a coefficient of variation mode for this sampler of from 41 to 50 percent.

Core Samplers--These sample soft stream substrates in the same manner as soil samples are collected. Although they reach deeper into the substrate than the Ekman grab, special techniques are often required to hold the sample in place during retrieval.

### Riffles--

The dominant substrate of riffles is rocks, ranging from pebble to boulder size. This habitat occurs where the stream gradient is steep, and ranges from gentle, shallow riffles occurring only occasionally along lowland, large rivers, to rapids and cascades occurring over entire reaches of mountain streams. Owing to the heterogeneity of habitat--the various size rocks will also entrap "microhabitats" of debris, gravel, sand and silt--and generally high oxygen content, the greatest diversity of organisms in a stream reach usually occurs in the riffle areas. The total biomass of invertebrates is generally also quite high in riffles, particularly when the water is rich in nutrients and the substrates are stable. The high heterogeneity of riffle habitats also increases the natural patchy distribution of the invertebrates over the habitat, thus increasing sampling variability.

Again, if "export" is relevant, it would probably be useful to separate the non-insect invertebrates and the riffle beetles from the remainder of the insects which "export" their biomass from the streams at emergence. Because mechanical grab samplers and corers are ineffective in rocky riffle substrates, sampling devices for riffles generally consist of some type of enclosed net sampler or colonization trap.

Enclosed Net Samplers--Absolute techniques involve enclosing a unit-area (usually 0.093 $m^2$) of substrate with a frame or box of which the upstream end is either open (Surber sampler) or consists of a fine-meshed netting [Portable Invertebrate Box Sampler (PIBS)] that allows the stream current to pass through the sampler. The downstream end of the sampler is always equipped with a fine-meshed net that collects the debris and organisms that have been dislodged through scrubbing of the substrate material of the enclosed area by hand. The Surber sampler is less adequate than the completely enclosed PIBS sampler because of loss of organisms through backwash. Disadvantages of these samplers are that they can be operated only in shallow waters (arm's length deep) and, like the Ekman, they do not sample deep into the substrate where a large proportion of the invertebrate biomass may be present (Hynes 1970). Weber (1973) reports a mode of coefficients of variability for the Surber sampler of from 41 to 50 percent. Efficiency of the enclosed net samplers varies greatly depending on ease of sampling, heterogeneity of habitat, and richness of biota. A cautionary note here: There may be a tendency to sample very close to the bank or where the water is shallowest because this may be the only area available for effective net operation. In streams that exhibit pronounced temporary fluctuation in discharge in accord with storms and water usage patterns, such shallow areas may yield unreasonably low estimates of biomass because they may have only recently been inundated.

Colonization Trap--Where the water is too deep for enclosed net samplers, a bag, tray, or box of known size is filled with cleaned substrate material from the riffle and allowed to recolonize over a period of about 6 weeks. The sampler is carefully retrieved so as to prevent escape of the fast-moving invertebrates (such as larger stoneflies which may make up a large proportion of the actual biomass.) The use of SCUBA techniques may be particularly effective. Artificial substrate samplers, such as a basket filled with ceramic spheres or a multiple-plate sampler, although effective for comparative studies, do not accurately duplicate the actual stream conditions and may give misleading biomass estimates.

Runs--

Except for mountain streams with very steep gradients, most stream reaches consist of alternating riffles and runs, with runs generally making up an increasingly greater proportion of the habitat as the stream gradient decreases. Unlike pools, water flows over runs, but often at a slow rate. The larger rivers and streams of lowlands consist almost entirely of runs. The substrate of runs ranges from coarse silt to sand to gravel. Because of the high instability of this substrate in flowing water and the abrasive nature of the particles, the invertebrate fauna of this habitat is usually extremely sparse. It is not uncommon to sample several square meters of substrate without finding more than a dozen organisms (normally midges, burrowing mayflies and dragonflies), and it is easy to see how misleading a biomass estimate would be if pool or riffle samples were used to estimate total stream biomass when much of the stream bottom consists of the "run" habitat. The most common sampling devices for runs are heavy, jawed grab samplers, such as the PONAR.

Grab Samplers--PONAR grab samplers operate similarly to the Ekman grab, but are designed to work effectively in sand or gravel. They are heavy samplers that are lowered on a cable from a bridge or boat with jaws that are held open and released at impact to "bite" the substrate. Because of the extremely low density of organisms found in sandy substrates, the patchy nature of invertebrate distribution can result in very high replicate-to-replicate variability of data. Therefore, extra caution is needed when estimating the invertebrate biomass of runs.

## Sampling Considerations

Chapter 12 of Hynes (1970) should be required reading for all investigators attempting to obtain stream macroinvertebrate biomass or standing crop estimates. The inherently heterogeneous nature of streams and the patchy distribution of the organisms over the substrate result in highly variable data. However, if the model in question accepts inherent natural variability of benthic invertebrate distribution and requires an allowance for error of about 50 or 100 percent, then three to five replicates should normally be adequate. Because the collection of benthic samples takes only a fraction of the time and effort involved in processing these samples, a safeguard strategy to assure that even this error (50 to 100 percent) is reached would be to collect a large number of samples (e.g. 5 to 10), and then process and analyze the replicates only until the desired level of error is obtained. This method is similar to the sequential sampling technique recently developed by pest entomologists (Resh 1979) and assures the desired level of error is reached with the minimum amount of processing effort. For additional information on required sample size for a given level of precision see the biometrics chapter in Weber (1973).

Consideration should be given to the variability of stream invertebrate biomass over time. Life cycle features of the dominant insect species present in a reach of stream can greatly influence the amount of biomass in the stream at any given time, as described by Hynes (1970). For example, in a stream dominated by spring mayflies, invertebrate biomass can fall sharply during late spring as many of the mature individuals emerge. Streams dominated by summer species of black flies and midges or by amphipods (which breed and grow during the summer months) may reach their peak in biomass during late summer. Thus, a "transport-fate" model that requires invertebrate biomass as an input should take these large seasonal fluctuations into account. This requires that benthic samples be taken from the stream reach in question on a seasonal basis to determine the amplitude and duration of the seasonal variations.

In addition to seasonal changes of biomass, less predictable but substantial changes occur on an annual basis. Hynes (1970) presents invertebrate data taken from a river station during the same season over a 9-year period that show that the total number or organisms changed as much as threefold from year to year. These changes are probably in part due to annual differences in intensity and timing of climatic events and features. Periods of high water often have an especially drastic effect on biomass, reducing it by several-fold. In the semiarid western United States, localized summer thunderstorms can produce extremely severe floods and substrate scouring, reducing the invertebrate populations from thousands per square meter to close to zero. In short, even with the most carefully designed sampling methodology, extreme caution is necessary when evaluating invertebrate biomass, and consideration must be given to the above factors.

## Processing Benthic Samples

Processing riffle and run invertebrate samples for biomass estimates will consist chiefly of extracting the invertebrates from the gravel and debris. Separation of debris and invertebrates from gravel is usually quick and simple. The sample is poured into a pan with water and swirled about with the lighter weight debris and organisms which collect at the top retained (gold-panning in reverse). This can be done in the field or in the laboratory. Before discarding the gravel, it is checked for snails, clams and stone-cased caddisflies. If present, they will have to be hand-sorted from the gravel component. Pool samples will consist of mud and some debris. The mud can be rinsed through a large fine-meshed sieve or a bucket especially equipped with a fine-meshed bottom.

Extraction of invertebrates from the remaining debris (sorting) is usually by far the most time-consuming and tedious task involved with invertebrate analysis and is normally done in the laboratory. Hynes (1970) reviews techniques which have worked with varying success to expedite the sorting. Weber (1973) also describes processing procedures for macroinvertebrate samples.

Subsampling, as suggested by Weber (1973), should also be considered as a means of greatly reducing processing effort. For purposes of estimating biomass, the entire sample should first be searched for the large, conspicuous organisms (dragonfly and stonefly nymphs, horse fly larvae, large caddisfly larvae, etc.). These will be quickly sorted and will often consist of the great majority of the biomass. The smaller organisms (of which there may be hundreds or thousands) can then be sorted from a fraction of the sample (e.g. 1/4 or 1/8) and the resulting biomass from this fraction back-multiplied by the reciprocal of the portion sorted and added to the biomass of the larger organisms which were sorted from the entire sample.

Naturally, the replicate samples must be kept discrete throughout the processing, so that the biomass values from these separate replicates are available for use in evaluating the variability among the replicate samples and, hence, the precision of the biomass estimate yielded by the sampling methodology employed. As noted earlier, it may also be important to separate invertebrates that emerge from the stream from those that do not, if biomass "export" is an input in the model. Also, recording the size distribution of the more important species will assist in determining whether biomass was increasing or decreasing at time of sampling.

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## Appendix B-2. Algal Sampling and Processing Procedures for Stream Environments.

### Periphyton

The three basic stream habitats (pools, riffles, and runs) can have a variety of substrate types (sand, pebbles, large rocks, aquatic plants, sticks, etc.) each with a unique periphyton community. Difficulties in making accurate estimates of periphyton biomass in streams are largely due to the variability of substrate types and current velocities. In some streams light can also be a very important controlling factor.

Periphyton on natural substrates is highly variable due to different textures and types of substrate, and the irregular surface is difficult to quantify. For these reasons artificial substrates have come into use as they seem to reflect the natural community clearly and are now accepted by most researchers (Weitzel et al. 1979). Sladeckova (1962) describes numerous natural and artificial substrates and gives detailed methods for their use.

On natural substrates, mason jar lids or pieces of sheet rubber with circular holes punched in them have been used to describe the area for sampling (Pers. Comm. with William D. Taylor, UNLV). The sheet rubber conforms to the shape of many substrates thereby increasing the accuracy of the sample. The substrate should be held over a pan while the periphyton are scraped or brushed from it. The area is then rinsed into the pan to ensure that all of the periphyton is included in the sample.

When using artificial substrates particularly good success with unglazed ceramic tiles in streams and fiber glass plates in lakes has been reported (William D. Taylor, UNLV Pers. Comm.). The ceramic tiles can be attached to concrete blocks or bricks with silicone rubber and are easily cut free after appropriate exposure. Lowe and Gale (1980) tested substrates for monitoring periphyton in deep rivers. They recommended frosted acrylic for future studies employing benthic artificial periphyton substrates. Weber (1973) recommends the standard (plain 25 x 75 mm) glass microscope slide as the most suitable artificial substrate for quantitative sampling.

### Phytoplankton

Phytoplankton can be collected with several types of sampling devices. Kemmerer and Van Dorn samplers collect known volumes of water (1, 2, and 3 liters are standard) from discrete depths. A tube sampler is designed to sample the entire water column to a depth equal to the length of the tube. This sampler integrates algae in the water column so that vertical layering information is lost, but it has the advantage of collecting all of the algae in the vertical segment of water. Phytoplankton nets (64 μm mesh) have been used for years to concentrate plankton algae from large volumes of water, but they cannot be considered quantitative samples suitable for obtaining biomass estimates. Unfortunately the small nanoplankton, which often constitute the bulk of the algal biomass, readily pass through the net and are lost from the sample.

All sampling for phytoplankton should take into account the vertical and horizontal patchiness of the plankton community to properly characterize the water body. A single sample taken from one depth at a station may totally misrepresent the actual overall conditions of the aquatic ecosystem being examined.

## Sample Preservation

A variety of solutions are available for the fixation and preservation of algal samples (Vollenweider 1969 and Weber 1973). It is the experience of Taylor et al. (1979) and that of others (Vollenweider 1969) that acid Lugol's solution is the fixative and preservative of choice for freshwater algae. Acid Lugol's solution is prepared by mixing 10 g iodine and 20 g potassium iodide in 200 ml of distilled water. To this, 20 ml of glacial acetic acid is added a few days prior to using. The solution should be stored in a dark bottle to reduce oxidation of the iodine. This solution is added to a sample at a 1:100 ratio. If large amounts of materials are collected in a sample, enough acid Lugol's solution should be added to maintain a tea color in the water. If samples are to be stored for more than 1 year, the preferred preservative is formalin (40 percent formaldehyde = 100 percent formalin), which has been neutralized with sodium tetraborate (pH 7.0 to 7.3). Five ml of neutralized formalin are added for each 100 ml of sample (Weber 1973).

## Estimating Algal Biomass

Various microscopic, gravimetric and chemical techniques are used to measure the quantity of algal biomass (APHA 1980). The following quantitative measurements can be made using microscopic techniques: numerical abundance, cell volume, cell surface area, and plasma volume. Common gravimetric and chemical procedures for measuring biomass include the following parameters: dry weight, ash-free dry weight, carbon, phosphorus, nitrogen, and chlorophyll *a*.

Direct microscopic examination provides the most useful kind of information (Fogg 1965) and has three basic advantages over other methods. The first is that the algae are observed each time a count is made so that any changes in appearance, size, shape, or aggregation of cells can be recorded. The second is that dead and living cells may be differentiated. Finally, exact information on algal species composition and size distribution is obtainable.

Non-microscopic determinations of algal biomass may be impaired by the presence of detrital material, particulate organic matter, zooplankton and bacteria, but are much less time consuming than microscopic counting methods. Except for pigment determination, non-microscopic methods are generally inferior for obtaining reliable biomass estimates and are not further discussed.

### Microscopic Methods--

Numerical abundance--The use of numerical abundance (cells/ml or cells/$cm^2$) is of limited value as a measurement of biomass. This is attributable to the variation in cell size within individuals of a species and between different species of algae. Cell counts do not express these differences since equal numerical value is assigned to each algal cell, regardless of size. Paasche (1960) reported that cell numbers tend to be biased towards the smaller, usually more numerous species in the community. Munawar et al. (1974) reported that cell numbers do not give information about phytoplankton biomass nor can they be correlated with primary production, particularly where algal populations are variable in size. However, cell numbers have been correlated with chlorophyll *a*. Taylor et al. (1979) found a rank correlation between cell numbers and chlorophyll *a* for 44 eastern and southeastern U.S. lakes to be 0.72 ($p < 0.01$). Munawar et al. (1974), also reported a significant correlation between cell abundance and chlorophyll *a* ($r = 0.59$, $p < 0.01$).

*Cell volume (Biovolume)*--Determination of cell volume ($\mu m^3$ per individual or colony) provides a measure of the algal biomass (mg fresh weight/$m^3$, assuming that the specific weight of algae is approximately unity. This measurement of standing crop is widely accepted in quantitative surveys (Rodhe et al. 1958, Nauwerck 1963, and Munawar and Nauwerck 1971). The appropriate dimensions of at least 25 randomly selected cells are measured, and the volume of *each* of the measured cells calculated, from which the mean cell volume *is* derived (Smayda 1965). The mean cell volume should not be calculated from the average linear dimensions of the individual cells. Cell volumes are usually reported in $\mu m^3/l$, or $\mu m^3$. Simple geometric formulae may be used to compute the cell volumes although some algal cells may have to be subdivided into several shapes because of their complex geometric configurations. Cell volumes are computed by simply integrating the volumes calculated for each form. Standard volumes from published sources should be used with great care in these calculations since differences in cell dimensions vary considerably from one place to another and even seasonally at the same place.

Results of phytoplankton surveys expressed in terms of biovolumes may tend to overemphasize the importance of the larger forms as producers (Paasche 1960). The small nanoplankton generally assimilate much more carbon per unit of biomass than the larger forms (Findenegg 1965).

Cell volumes generally provide good correlations with other biomass parameters. Munawar et al. (1974) reported that cell volume was better correlated to chlorophyll *a* than cell surface area and numerical abundance. Taylor et al. (1979), however, reported better correlations with cell numbers and chlorophyll *a* than biovolumes and chlorophyll *a* (rs = 0.72 and 0.66, respectively). Cell volumes can be converted to biomass using the following formula from Strickland (1960) and Lund and Talling (1957).

$$\text{Biomass (mg)} = V_{\text{total}}\ (\ m^3) \times 10^{-9}\ \frac{\text{mm3}}{m^3} \times S,$$

where: $V_{\text{total}}$ = sum of the volume for each species, and S is 1.0, the approximate specific gravity of algae.

The results of most surveys are expressed in terms of fresh weight (mg) where the approximate specific gravity of algae is assumbed to be 1.0 (Rhode et al. 1958).

*Cell surface area*--Cell surface area (μm$^2$) provides a better method of estimating standing crop than numerical abundance; however, it is not as widely used or as quantitative as cell volume (Munawar et al. 1974). Cell surface area is important since it represents the assimilative area for pollutants or nutrients. The area computation is similar to the method used in computing cell volumes.

### Nonmicroscopic Methods for Plant Pigment Measurements--

Chlorophyll *a* is the predominant chlorophyll pigment in algae and assumes considerable importance in standing crop estimates. The speed and simplicity of chlorophyll *a* analysis are the two main reasons that this method is the most popular for estimating standing crop (Strickland 1960). Results are usually reported in g/l or g/cm$^2$. The analysis is far less time consuming than the microscopic "counting" methods; however, it does not furnish information on algal species and size composition. This method of estimating biomass is also faced with certain problems, i.e., pigment extraction is not always complete, chlorophyll content varies with the age and light or shade adaptation of the population, relative pigment composition of various algae groups is not always constant, and degradation products may be present that are extracted along with active chlorophyll by ordinary extraction processes. Kalff and Knoechel (1978) provide the following formula for converting algae fresh weight to chlorophyll a:

$$\text{Chlorophyll } \underline{a} \text{ (mg)} = F \times \text{fresh weight (mg)},$$

where:

F = 0.006 to 0.008 when the community is dominated by Cryptophyta, and
F = 0.003 when the community is dominated by diatoms.

Chlorophyll *a* data are especially informative when used in conjunction with other biomass parameters (Fruh et al. 1966). Weber (1973) and APHA (1980) provide descriptions of appropriate procedures for chlorophyll *a*, b, c and phaeophyton determinations using fluorometric annd spectrophotometric methods.

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## Appendix B-3. Fish Sampling Methods

### Population Estimates

Total population estimates, including species and size class distribution data, would be required to provide a precise estimate of the amount of a given toxic organic substance potentially bound in fish tissue in a particular stream segment at any given moment. Such precision is unnecessary given the present state of predictive fate and transport models because they are not sufficiently refined to accept this level of input data. However, in anticipation of further refinement of predictive models it behooves the biologist to obtain the best population estimate possible that is consistent with economic effort and model sensitivity and resolution.

Inasmuch as it is generally impractical to attempt to obtain complete counts or absolute biomass measures by size class and/or species in most fisheries surveys, the biologist must attempt to obtain reasonable estimates of these parameters based on samples of the population. Such estimates are especially difficult in large rivers as pointed out by Cleary and Greenbank (1954).

> "On the whole, a large river probably contains a less uniformly distributed fish population and a less stable one, in any given locality, than does either a lake or a small stream. Thus, it is extremely difficult to make a quantitative population estimate of the entire river, or even of a sizeable stretch of it, by sampling random localities at random times, unless a formidably large number of samples is taken. The task is made all the more difficult by the fact that most known sampling devices do not take a non-selective sample even in the immediate locality in which they are operated.
>
> Finally, it must be taken into consideration that the total population changes from day to day, season to season, and year to year. Recruitment comes about by the hatching of young, ingress, and by artificial stocking. Removal is by angling, commercial fishing, predation, death by natural and unnatural causes, and exodus into connecting waters."

Commenting on the adequacy of "complete" counts in large stream, i.e., actual counts of all or nearly all individuals in a population, Cleary and Greenbank (1954) noted the following:

> "The physical nature of large streams usually precludes bringing to hand the entire fish population, except in special instances, such as the counting of fish at a fishway during spawning migration. However, the idea of a total count may be applied to a given portion of a stream. This portion then becomes a whole, in a sense, and may even be considered a "body of water." For instance, a section of a stream is blocked off and a population count made with an electric shocker. Probably this count should more properly be considered a complete enumeration of the

population of that stream section rather than a random sample of the entire stream's population."

For purposes of obtaining total population or biomass estimates for large segments of streams; extrapolation of "complete" count data from small representative sections to large reaches warrants consideration. The advantages and disadvantages of this approach will have to be examined on a case by case basis. If small stream segments that are representative of larger reaches can be clearly delineated and adequately sampled, this technique could prove very effective.

To obtain "complete" counts, the portion of the stream to be sampled would have to be completely blocked to prevent ingress and egress of fish in the area. The most common technique for blocking a section invloves the placement of seines at each end of the segment to be sampled. Obviously, small, slow moving, streams can be more effectively blocked in this manner than large, swift streams. Drifting objects, boat traffic, etc., seriously interfere with this technique in large systems.

A number of options are available for actually collecting the fish in a complete count survey. Many of the sampling previously discussed by Weber (1973) and Bagenal (1978) could be used singly or in combination with others for such purposes. In very small streams with relatively uniform channels and little rooted vascular plant growth, seining techniques are effective provided obstructions that would interfere with the operation of the seine or provide refuge for the fish are absent or are removed prior to the operation. Drag seines have been used for years for obtaining population estimates as well as for qualitative work. Hoover (1938) blocked off portions of small trout streams and a large crew attempted complete removal inside the blocked off areas. Seining efficiency, as indicated by the mark and recapture method plus dynamiting, ranged from 70 percent to 100 percent depending on the number of obstructions in the area. Gerking (1949) reported a seining efficiency of 88 percent based on his work with a drag seine in a small warm-water stream in Indiana.

Despite these efficiencies with seines, Cleary and Greenbank (1954) regard shocking as the most generally effective method of obtaining entire population counts of sections of a stream or entire small streams. Poisons and narcotizing agents are also effective for removing fish from entire sections, but an obvious disadvantage is the hazard posed to fish downstream from the experimental area. Even if attempts to completely remove fish from stream segments are successful, extrapolation of the data to large stream reaches is a potential source of considerable error in biomass estimates. If the segments sampled are truly representative of the entire reach under investigation, a direct linear extrapolation of the biomass data is easily accomplished through application of a proportional factor. This is the simplest and most direct approach and probably is adequate for most survey purposes. This assumes that the area (or volume) of each habitat within the experimental section or sections sampled, is in direct spatial proportion to the actual occurrence of each habitat throughout the entire section for where biomass estimates are sought. If individual habitats, e.g., pools, runs, riffles, weed beds, etc., are blocked off and sampled, the percentage of stream reach comprised by each habitat will have to be determined and the biomass data applied proportionally. The investigator will have to make the decision as to whether biomass data are reported for each species, for groups of species and size classes occupying similar habitats, or by some other system. Typically in streams supporting diverse fisheries different habitats will be occupied by different species with fair consistency. Length and weight measurements and size class grouping of each species should provide the level of information required in practically all surveys.

Complete fish counts for a stream section or individual habitat may often be impossible to obtain, particularly in large, deep, and/or fast moving streams. For this reason, the method of "mark and recapture" is usually employed for estimating populations. This procedure involves marking (e.g., by fin clip, tag, or dye) all fish in a catch and releasing them. In a subsequent catch the number of fish with marks (i.e., "recaptures") and without marks are noted and by simple proportion, a population estimate achieved. For a complete description of this method, including the formula for computing standard error of the population estimate, biases inherent in the procedure, and methods for minimizing these biases, refer to Chapter 6 "Estimation of Population Number and Mortality Rates" in Bagenal (1978).

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## Appendix B-4. Macrophyte Sampling Methods.

### Qualitative Sampling--

Samples of macrophytes are gathered by hand, with grappling devices, rakes or dredges. Plants collected for analyses of cumulative substances should be removed in their entirety including flowers, seed pods, roots, rhizomes and tubers if possible. Representatives of all major communities should be collected and placed in appropriate containers and frozen for storage and shipment. Generally, identification of most common species can be made in the field by an experienced aquatic biologist with the aid of appropriate taxonomic keys. Rare or questionable specimens can usually be identified by a macrophyte taxonomist if the specimens are handled properly during and following collection. Two common references that provide taxonomic treatment of aquatic vascular plants are Fassett (1968) and Muenscher (1944).

### Quantitative Sampling--

Quantitative sampling of macrophytes for purposes of obtaining biomass estimates for an entire stream reach or section thereof is a laborious task. A critical aspect of such an undertaking is the accurate mapping of the stream reach for purposes of delineating vegetative zones or plant communities. The investigator can exercise considerable judgement and personal preference in the delineation of plant zones regarding the number and sizes of discrete zones. The important consideration is that the community boundaries be clearly defined and plotted on scale maps as accurately as possible. Communities may be delineated based on growth patterns (e.g., submersed, floating, emersed), density of stand (abundance), diversity or "purity" of stands or a combination of these characters. "Limnological Methods" (Welch 1948) is a good reference for conducting stream surveys, and for determining areal extent of designated vegetation zones through the use of planimetry.

The sampling design should be such that the total biomass within each designated zone can be estimated and expressed on a wet weight per unit area basis. Sampling procedures involve the establishment of transects or grids following procedures adapted from terrestrial plant survey techniques. The following references will be useful for this purpose: Edwards and Owens (1960), Forsberg (1959), Boyde (1969), and Westlake (1966).

The actual sampling may involve wading, use of boats or diving. Plant material may be removed by hand or by a sampling apparatus, depending upon the nature of the substratum, water depth, and the type of plant communities being sampled.

Determination should be made prior to initiation of sampling as to what portion of the plant material is considered within the quadrant, e.g., all plant material rooted within the quadrant, all plant material within the sampled projections of the quadrant, etc. The sampling protocol should also specify whether the entire plant will be removed intact or whether portions above the substrate will be removed and the roots removed separately.

All sampling techniques and equipment have their limitations. Grabs such as the Ekman or PONAR can be used in relatively deep waters. They sample small areas, but they are inconsistent with respect to the amount of root material removed, and it is very difficult to restrict the sampling to the confines of a quadrant. Corers are efficient for sampling roots in mud, sand and small gravel, but they are not effective samplers of leafy plant material.

SCUBA techniques are very useful in many streams enabling the investigator to remove all materials within the confines of a quadrant with direct "hands on" contact. Turbidity may impede visibility of the divers even though sufficient light penetrates to permit plant growth.

Plant materials retrieved are typically accompanied by large quantities of soil, epiphytes and attached animals. Removal of soil requires that the plants be washed over a sieve in a stream of water, but this also removes most of the epiphytes and associated fauna. Estimates based on the work of Odum (1957) and Edwards and Owens (1965) indicate that the weight of epiphytes alone may be of the same order as the weight of macrophytes to which they are attached.

Advances in remote sensing techniques are encouraging in terms of their potential for providing biomass estimates of plant materials. Techniques range from the use of aerial photography to define the spatial distribution of plant beds to the use of laser fluorescence devices for estimating the quantities of plant pigment in a given volume of water. Pigment concentrations can then be related to standing crop or biomass. Currently remote sensing techniques are in the developmental stages for purposes of providing quantitative standing crop estimates on an aerial unit basis.

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## Appendix B-5. Invertebrate Drift Sampling Methods.

Typically, sampling drift organisms involves the use of specially designed nets anchored just above the stream bottom (but below the surface in shallow streams). Drift nets are left in place for a few minutes up to 24 hours depending upon the density of organisms and amount of floating debris in the water. Results are expressed in terms of biomass or number of animals captured per unit time, and, if desired, composition of the fauna can be determined. For further discussions of sampling procedures for drift organisms see Weber (1973), Elliott (1970), Waters (1962, 1969) and Edmondson and Winberg (1971).

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## B-6. Zooplankton Sampling Methods.

Zooplankton biomass in the water column of deeper streams can be estimated by using appropriate mesh netting [No. 10 (0.158 mm) for microcrustacea and No. 20 (0.076 mm) for rotifers and nauplii]. Of course, the finer mesh netting which clogs very rapidly in many streams is best used at some distance above the substrate, whereas much coarser macroinvertebrate sampling net material (0.5 mm) is better suited to use near the stream bottom where most of the coarser suspended material is transported.

Conventional zooplankton sampling techniques, both quantitative and qualitative, may be appropriate for very large streams. These procedures involve the use of metered tow nets deployed from boats and drawn through water either horizontally or vertically, as well as filtering water collected in containers or pumped to the surface. Weber (1973), Welch (1948), and Edmondson and Winberg (1971) provide descriptions of zooplankton sampling apparatus and their uses for a variety of sampling situations and study objectives.

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